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Optical and structural characteristics of strontium doped calcium tartrate crystals

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Abstract. We report here on the optical and structural characteristics carried out on strontium doped calcium tartrate tetrahedral single crystalline materials obtained by diffusing calcium and strontium ions through silica gel impregnated with optically active tartaric acid. Linear optical properties of this material such as refractive index, birefringence and transmission characteristics were measured in the wavelength range 200 nm $< \lambda <$ 1500 nm. No dispersion of the birefringence was observed within the experimental accuracy. The packing of tartrate molecules remained unaltered with 12% of the strontium doping.

Keywords. Silica gel; refractive index; crystal structure; second harmonic generation.

1. Introduction

Single crystals of calcium tartrate (CT) and strontium tartrate (ST) have attracted considerable attention in recent years on account of their ferroelectric, non linear optical and spectral characteristics (Medrano *et al* 1987; Brehat and Wyncke 1989; Nakatani 1991; Selvarajan *et al* 1993; Rethinam *et al* 1994). CT and ST crystallize in the orthorhombic system with space group $P2_12_12_1$ having four molecules in the elementary unit cell (Ambady 1968; Bohandy and Murphy 1968). In the course of our investigations on the physical properties of CT and ST our attention was drawn to the growth and characterization of strontium doped calcium tartrate (CST). This work was undertaken to study the optical characteristics and effect of doping on the structural role of tartrate ion in the presence of two divalent metallic elements.

2. Experimental

2.1 *Growth and crystal habit*

The strontium doped calcium tartrate single crystals employed for optical and X-ray diffraction studies were grown by the silica gel method. The growth process involves the controlled diffusion of calcium chloride–strontium chloride solutions into gel made up of sodium metasilicate and tartaric acid (all AR grade) solutions at constant temperature and visible light conditions. The experiment was performed in Corning glass tubes of length 200 mm and inner dia. 25 mm. The suitable conditions for the growth of the best quality CST single crystals were: pH 3·5–4·0, gelling time 12 days, concentration of the reactants 1·0 M and growth temperature 30°C. Growth of CST crystals (about $10 \times 6 \times 4$ mm^3 in size) was observed down the gel column in the experimental vessels within a week. During the exchange reaction HCl yielded as a byproduct. The crystal size and time of formation of ST depend on the density of the gel and concentration of the supernatent solutions. The gel grown CST single crystals were colourless and optically transparent. Qualitative chemical analyses using an energy dispersive X-ray spectrometer (EDX) confirmed that the single crystals are those of CST in which two alkaline earths form solid solution in the ratio 0·88 : 0·12. The maximum uptake of strontium in the CST crystal depends on the molarity of the mixed calcium chloride and strontium chloride solutions with different ratios. The crystals grown were confirmed to have the composition $Ca_{0.88}Sr_{0.12}C_4H_4O_6 \cdot 4H_2O$ under the above mentioned growth conditions. The single crystalline habit of CST is deviated from the habit of CT and ST single crystals (figure 1). The crystals are elongated in the b-direction and the principal faces are (110), (010) and (011) with their symmetry equivalents.

2.2 *Structure*

The crystal thus grown was transparent and was mounted on the X-ray diffractometer after confirming the quality by examining under a polarizing microscope. The intensity data were collected on an Enraf–Nonius CAD4 diffractometer having graphite monochromated MoKα radiation ($\lambda = 0{\cdot}7107$ Å) in the $\omega/2\theta$ mode. The cell parameters were obtained from the least square refinement of 25 reflections ($-2\,3\,1$, $-1\,3\,0$, $0\,3-1$) after every 3600 s

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of exposure time; the orientation was checked every 400 reflections and no significant fluctuations in their intensity were observed. The data was corrected for Lorenz and polarization effects but not for absorption effect since it is negligible. The structure of strontium doped calcium tartrate tetrahydrate was solved using SHELXS 86 (Sheldrick 1985). The heavy atoms were located using Patterson method and the rest of the structure was developed using partial structure expansion technique. The structure refinement was carried out using SHELX 93 (Sheldrick 1993). Hydrogen atoms were located from the difference map. All nonhydrogen atoms were refined anisotropically. The details of crystal data and refinement results are given in table 2.

3. Results and discussion

3.1 *UV-visible spectrum of CST single crystals*

Optical absorption measurements for CST single crystal with thickness 1·0 mm were performed with a Cary-14 spectrophotometer in the range 200–1400 nm at room temperature. No absorption decreasing film was coated on the surfaces of the crystal and the light loss caused by reflections on the surfaces was ignored. The absorption coefficient as a function of wavelength, was evaluated. Anisotropy was observed for different light directions. One can see from figure 2 that the single crystals of CST are transparent in the range 275–1325 nm and the transmittivity is greater than 85%. The optical transmission range as determined from the optical characteristics, makes the CST crystal interesting for second harmonic generation in the ultra violet region.

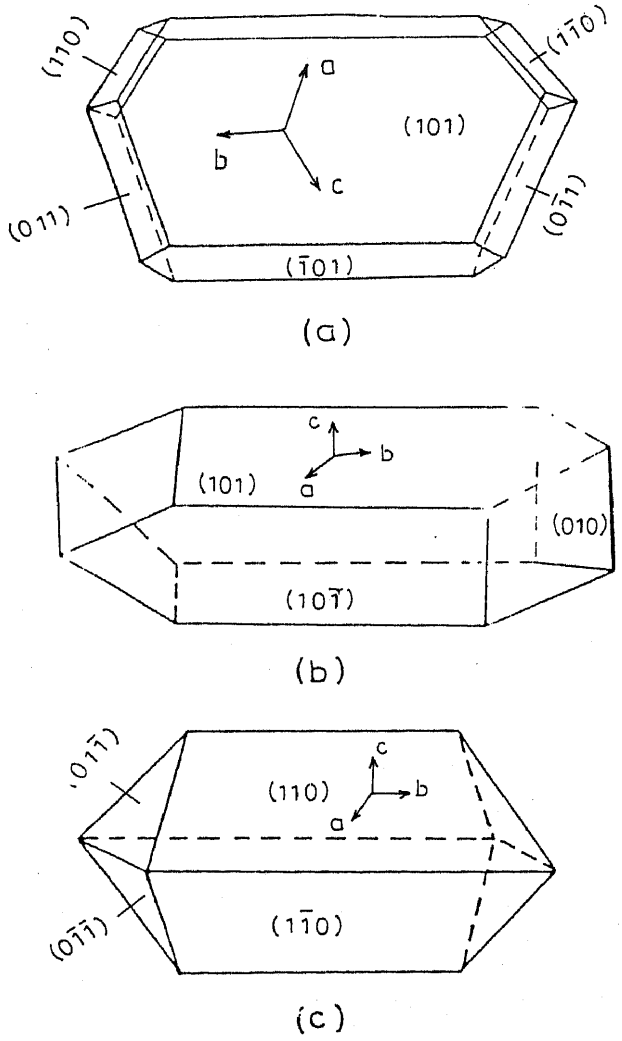

Figure 1. Habit of (**a**) calcium tartrate, (**b**) strontium tartrate and (**c**) strontium doped calcium tartrate single crystals.

3.2 *Linear optical properties*

According to the crystal system three planes normal to the three orthorhombic unit cell axes with x, y, z parallel

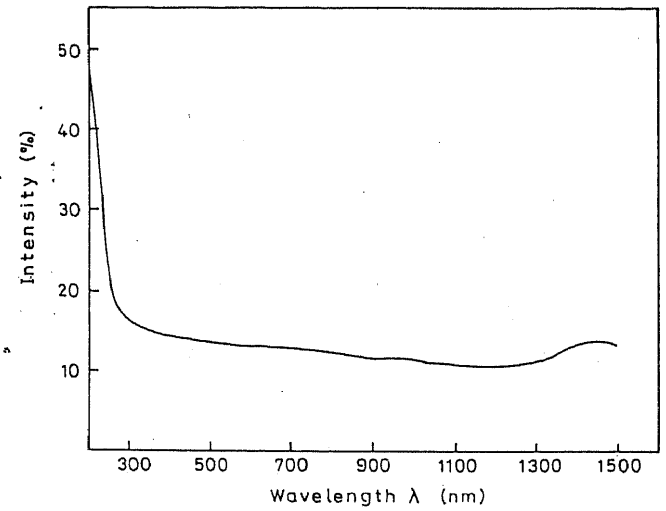

Figure 2. UV visible spectra of strontium doped calcium tartrate single crystal (thickness, 1·0 mm).

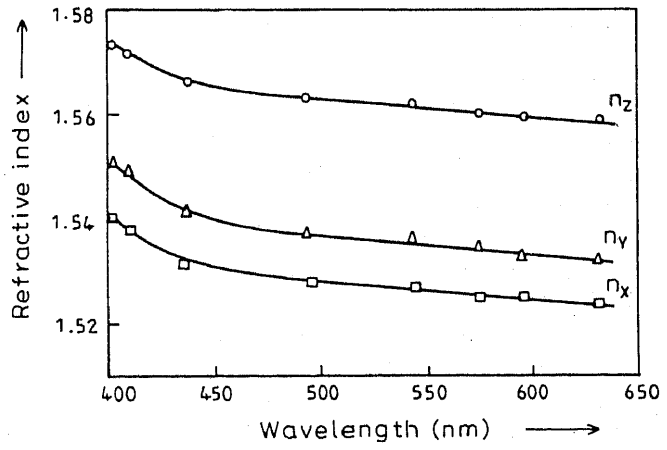

Figure 3. Dispersion of the principal refractive indices of strontium doped calcium tartrate single crystal at room temperature.

to the crystallographic a, b and c axes, respectively, were prepared to determine birefringence and refractive indices. The refractive index of the crystal within the visible light range was measured by the Brewster's angle method (figure 3). The data are listed in table 1. The quality of the crystal together with the low birefringence of this material led to a precise measurement with an accuracy of ±0·005. The wavelength dependence of the birefringence was determined by using a monochromator, mercury lamp, sodium lamp and He–Ne laser as light source for the polarizing microscope. The birefringence is independent of the wavelength in the wavelength range 400–650 nm.

Table 1. Linear optical data of CST single crystals.

	Refractive indices			Birefringence	
λ (nm)	n_x	n_y	n_z	Δn_x	Δn_z
405	1·5398	1·5514	1·5738	0·02	0·03
408	1·5383	1·5501	1·5726	0·02	0·03
436	1·5316	1·5431	1·5661	0·02	0·03
492	1·5292	1·5392	1·5639	0·02	0·03
546	1·5272	1·5378	1·5632	0·02	0·03
577	1·5255	1·5356	1·5611	0·02	0·03
589	1·5243	1·5344	1·5589	0·02	0·03
633	1·5229	1·5336	1·5567	0·02	0·03

Table 2. Crystal data and structural refinement.

Empirical formula	$Ca_{0·876}Sr_{0·124}C_4H_{12}O_{10}$
Formula weight	266·11
Crystal size (in mm)	0·41 × 0·12 × 0·18
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	
a	9·231(2) Å
b	9·619(4) Å
c	10·610(5) Å
Volume	942·2(6) Å^3
Z (number of molecules per unit cell)	4
F (000)	576·0
Density (calc)	1·875 g/cm^3
Radiation used	Mo Kα (λ = 0·7107 Å)
Diffractometer	Enraf–Nonius CAD4
Diffraction measurement method	$\omega/2\theta$
Reflections collected	2284
Unique reflections	2027
2θ range	2·86° to 26·97°
h, k, l range	$-11 \le h \le 11$ $0 \le k \le 12$ $0 \le l \le 13$
Refinement method	Full matrix least squares on F^2
Goodness of fit on F^2	1·587
Final R indices ($I > 2\sigma(I)$)	R = 0·087, wR = 0·233
R indices (all data)	R = 0·152, wR = 0·268
Residual electron density	max = 0·83 e/Å^3, min = −0·58 e/Å^3

CST belongs to one of the four acentric orthorhombic point groups, determined by the convention that the principal refractive indices are such that $n_z > n_y > n_x$, which implies that in CST crystal the optical plane is the x–z plane. Results on the dispersion of the indices of refraction show that CST is an optically positive biaxial crystal.

3.3 *Non linear optical properties*

The second harmonic generation experiments were performed with an unfocussed and linearly polarized, Nd : YAG laser (λ = 1·064 μm). CST crystal exhibits small optical nonlinearity. The second harmonic generation intensity of CST is 0·1 times that of quartz. Limited by the experimental condition, the nonlinear optical coefficients of CST single crystal have not been obtained.

3.4 *Structure*

There is no significant structural change in the CST

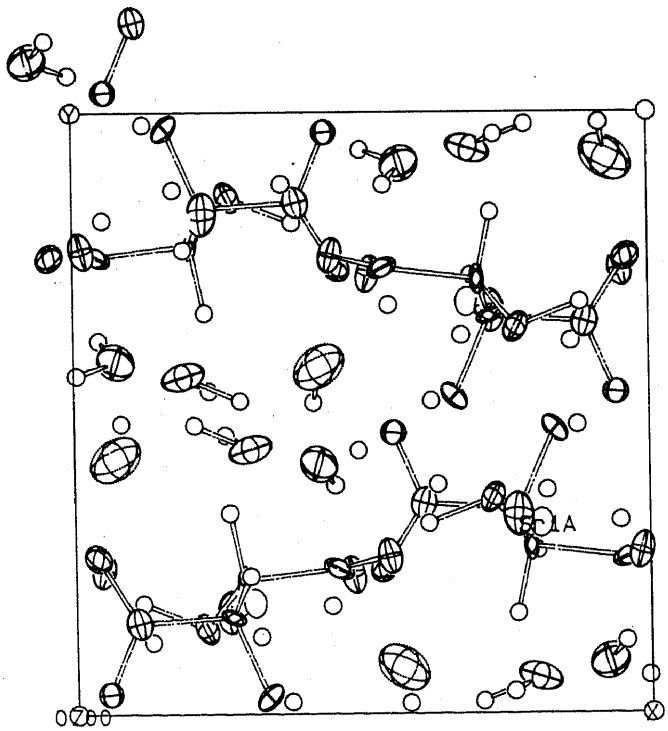

Figure 4. The structure of strontium doped calcium tartrate single crystal.

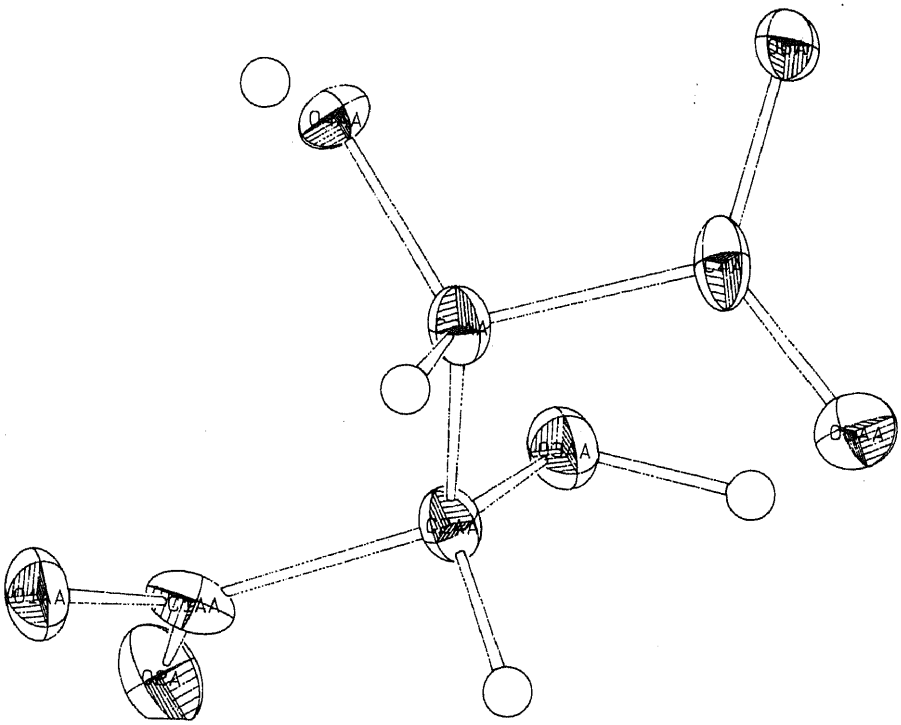

Figure 5. The details of the tartrate molecule.

Table 3. Atomic coordinates, occupancy and U_{eq}.

	x/a	*y/b*	*z/c*	Occupancy	U_{eq}
Sr	0·1864(2)	0·8160(2)	0·8218(2)	0·124	171(4)
Ca	0·1864(2)	0·8160(2)	0·8218(2)	0·876	171(4)
01	0·4507(8)	0·7617(8)	0·8086(8)	1·000	209(1)
02	0·0153(8)	0·7688(9)	0·9920(9)	1·000	273(6)
03	0·7717(8)	0·6415(8)	0·9517(8)	1·000	198(6)
04	0·6627(8)	0·5273(8)	0·7168(8)	1·000	219(0)
05	−0·0389(8)	0·7583(9)	0·7143(8)	1·000	222(8)
06	0·0573(8)	1·0334(7)	0·8275(9)	1·000	221(4)
07	0·1928(12)	0·5604(9)	0·8296(13)	1·000	552(6)
08	−0·0732(11)	1·0854(10)	1·0702(10)	1·000	404(0)
09	0·2269(9)	0·8309(11)	0·5877(8)	1·000	329(8)
010	0·4285(14)	0·5763(12)	0·5668(12)	1·000	624(6)
C1	0·5407(12)	0·7405(11)	0·8927(11)	1·000	200(0)
C2	0·7049(11)	0·7216(11)	0·8612(10)	1·000	172(4)
C3	0·7245(11)	0·6604(10)	0·7293(10)	1·000	119(9)
C4	0·1095(11)	1·1503(11)	0·7979(11)	1·000	177(8)
H1	0·88270	0·68360	0·95580	1·000	
H2	0·72970	0·83370	0·85550	1·000	
H3	0·69380	0·72880	0·65570	1·000	
H4	0·62410	0·52030	0·67590	1·000	
H5	0·29020	0·52030	0·86380	1·000	
H6	0·23640	0·53680	0·76380	1·000	
H7	−0·04380	1·12040	1·16000	1·000	
H8	−0·00440	1·06240	0·98000	1·000	
H9	0·17630	0·87130	0·60350	1·000	
H10	0·36640	0·88110	0·60310	1·000	
H11	0·41840	0·51760	0·48280	1·000	
H12	0·55200	0·67930	0·53880	1·000	

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 4. Anisotropic thermal parameters ($Å^2 \times 10^4$).

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca	126(8)	209(9)	178(9)	0(9)	3(9)	−7(9)
Sr	126(8)	209(9)	178(9)	0(9)	3(9)	−7(9)
01	149(35)	313(40)	166(42)	−29(36)	−2(35)	46(35)
02	165(38)	359(53)	297(50)	21(38)	−24(36)	−60(35)
03	160(37)	228(43)	207(42)	−62(32)	−43(32)	70(29)
04	163(42)	167(39)	328(48)	−78(32)	−76(34)	−84(31)
05	178(39)	197(39)	294(51)	−93(35)	−11(35)	98(50)
06	154(36)	148(35)	362(53)	6(38)	109(40)	−1(30)
07	529(66)	198(46)	932(92)	−55(57)	−112(79)	98(50)
08	373(53)	334(52)	506(69)	−162(45)	40(49)	46(42)
09	244(44)	491(57)	254(46)	−165(46)	27(35)	3(45)
010	680(78)	557(73)	637(88)	−153(59)	−311(68)	212(61)
C1	218(57)	108(49)	274(69)	51(46)	56(52)	76(48)
C2	59(49)	218(58)	240(56)	65(40)	72(42)	−15(39)
C3	154(50)	63(50)	142(50)	61(37)	−8(38)	58(37)
C4	156(52)	257(66)	120(57)	−99(42)	−17(44)	−27(43)

The anisotropic displacement factor exponent takes the form $-2\pi^2[(ha^*)^2U_{11}+\ldots+2hka^*b^*U_{12}]$.

Table 5. Interatomic distances (Å) in strontium doped calcium tartrate tetra hydrate.

Ca(Sr)–O6	2·407(7)
Ca(Sr)–O5	2·436(8)
Ca(Sr)–O2	2·441(9)
Ca(Sr)–O7	2·461(8)
Ca(Sr)–O4	2·498(8)
Ca(Sr)–O1	2·499(7)
Ca(Sr)–O9	2·516(9)
Ca(Sr)–O3	2·561(8)
O1–C1	1·236(14)
O2–C1	1·249(14)
O3–C2	1·377(13)
O3–Ca(Sr)	2·561(8)
O3–H1	1·103(8)
O4–C3	1·408(12)
O4–Ca(Sr)	2·498(8)
O4–H4	0·565(8)
O5–C4	1·233(13)
O6–C4	1·263(13)
O7–H5	1·044(11)
O7–H6	0·837(13)
O8–H7	1·046(10)
O8–H8	1·170(10)
O9–H9	0·630(9)
O9–H10	1·385(8)
O10–H11	1·059(11)
C1–O2	1·249(12)
C1–C2	1·563(15)
C2–C3	1·530(15)
C2–H2	1·104(10)
C3–C4	1·562(14)
C3–H3	1·060(10)
C4–O5	1·233(13)
C4–C3	1·562(14)

Table 6. Selected bond angles (degrees).

C2–O3–H1	103·8(7)
C3–O4–H4	115·8(10)
H5–O7–H6	77·0(9)
H7–O8–H8	131·7(10)
H9–O9–H10	116·2(11)
H11–O10–H12	104·2(9)
O1–C1–C2	121·1(10)
O3–C2–C1	110·5(9)
C1–C2–H2	95·7(9)
C1–C2–C3	110·8(8)
O3–C2–H2	119·5(9)
O3–C2–C3	111·7(8)
C3–C2–H2	107·5(9)
O4–C3–C2	112·9(8)
C2–C3–H3	113·8(9)
O4–C3–H3	112·8(9)
O7–H5–H6	43·6(7)
O7–H6–H5	59·4(8)

when compared with calcium tartrate (Hawthorne *et al* 1982). The crystal structure is shown in figure 4. Atomic coordinates and anisotropic thermal displacement parameters are given in tables 3 and 4, respectively. Interatomic distances, selected bond angles and hydrogen bond lengths are given in tables 5–7. The metal ion is coordinated by eight oxygens forming a distorted Siamese dedicahydron (Johnson 1966). The water molecule connects tartrate motifs by hydrogen bonding hence forming an infinite chain which runs along the a-axis. The adjacent chains are linked along b-axis by the metal and tartrate oxygen bonds. We conclude from this study that the packing of tartrate molecules remains unaltered with 12% of the strontium doping. Details of the tartrate molecule are shown in figure 5.

4. Conclusion

The silica gel growth system involves the use of calcium chloride and strontium chloride as the top reactants and sodium meta silicate impregnated with tartaric acid as

Table 7. Hydrogen bonds.

A–H . . . B	A–H	A . . . B	H . . . B	A–H . . . B
O4–H4 . . . O10	0·565(8)	2·725(15)	2·211(13)	152·5(8)
O7–H5 . . . O1	1·044(11)	3·077(13)	2·816(8)	94·4(5)
O8–H8 . . . O2	1·170(10)	3·261(13)	2·833(9)	100·8(5)
O8–H8 . . . O6	1·170(10)	2·887(14)	1·738(9)	166·0(6)
O9–H9 . . . O5	0·630(9)	2·882(11)	2·551(8)	115·8(9)
O9–H10 . . . O1	1·385(8)	3·194(11)	2·584(8)	103·0(4)
O3–H1 . . . O2	1·103(7)	2·596(11)	1·522(8)	162·8(5)
O3–H1 . . . O5	1·103(7)	3·266(11)	2·758(8)	107·6(5)

lower reactant results in the crystallization of calcium strontium tartrate with the molecular formula $Ca_{0.88}Sr_{0.12}C_4H_4O_6 \cdot 4H_2O$. The optical transition range has been determined from the UV-visible spectra for CST which extends from 275 nm to 1400 nm. This makes the CST material interesting for second harmonic generation in the UV region. The optical characteristics of CST crystal is found to be positive. CST exhibits optical nonlinearity. From the structural study, it is found that the packing of tartrate molecules remains unaltered with 12% of strontium doping in CST.

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