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Dedicated to Prof. Menachem Steinberg on the occasion of his 65th birthday

SOL-GEL PREPARATION AND FLUORINE SUBSTITUTION OF BiSCCO HIGH-T_c SUPERCONDUCTORS

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Abstract

Sol-gel citrate technology was used to prepare BiSCCO 2223 and 2212 superconducting phases. Fluorine in the initial mixture was shown to enhance considerably formation of the 2223 phase. Fluorine substitution of up to three F atoms per Bi(Pb)SCCO 2223 formula was achieved by treatment of the sample in 80 Torr ClF_3 atmosphere. A number of experimental methods have been used to characterize the samples and to trace the phase transformations in the sol-gel process: DTA/TG, XRD, atomic absorption, potentiometry with fluoride selective electrode, magnetic susceptibility measurements.

Keywords: BiSCCO synthesis, fluorine substitution, sol-gel

Introduction

Ever since the discovery of high temperature superconductivity in oxides great effort has been invested in the preparation of substituted derivatives. The majority of publications deals with cation doping, although anion substitution was also reported. In particular, attempts have been made to introduce fluorine into different types of HTSC: Ln_2CuO_4 [1, 2], YBCO [3, 4], BiSCCO [5–11]. Fluorine substituted BiSCCO has been prepared mainly by solid state reactions with or without subsequent vapor phase treatment. Only in one publication (Kemnitz *et al.* [11]) a different technique (freeze drying) was applied for that purpose.

In this paper the sol-gel method of preparation of BiSCCO 2212 and 2223 compounds was studied and fluorination of Bi(Pb)SCCO 2223 was made by means of ClF_3 treatment of the material at several temperatures.

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Experimental

Preparation

Sol-gel citrate technology was applied since this method has been successfully used in this laboratory and elsewhere for preparation of BiSCCO compounds [12–14]. The starting materials were the corresponding nitrates and PbF_2 (or PbF_2+CuF_2). The fluorine concentrations in the initial mixture were up to two atoms per formula. The mixture of salts was dissolved in nitric acid (1:20). Citric acid and ethylene glycol were added to the solution at the molar ratio 2:1 (two mols both of citric acid and ethylene glycol to one mol of the sum of the cations). The mixture was heated on a hot plate with a magnetic stirrer at 353 K for about one hour, until a blue viscous gel was formed. It was then pyrolysed at 473–773 K. At this stage spontaneous combustion of organics was observed and brown-to-black flakes of a fine particle material was formed. This residue was pulverized and calcined at 773 K for three hours, then reground and calcined for a further three hours at 1073 K to ensure elimination of the organic components. The resulting powder was pressed in vacuum to pellets 12 mm in diameter with a load of 10 tons at room temperature and sintered at 1113 to 1133 K for 24 to 210 h with intermediate regrinding and repelletizing. For fluorine substitution a static system was used. The Bi(Pb)SCCO 2223 powder sample was placed on a Pt dish in the reactor, pumped overnight and heated to 423, 473 and 523 K in vacuum for two hours. After that 80 Torr of purified and dried ClF_3 was admitted into the reaction vessel, the sample was held at these conditions for 60 min, cooled down to room temperature and pumped.

Characterization

The samples were characterized by XRD and DTA/TG. The cations were analyzed by atomic absorption (Perkin-Elmer 403 Atomic Absorption Spectrophotometer), and the fluorine concentration was measured by means of potentiometry with a standard fluoride selective electrode. Superconductive transition was characterized by magnetic susceptibility measurements. X-ray diffraction patterns were recorded on a Philips X-Ray Powder Diffractometer with CuK_α radiation. Simultaneous differential thermal analysis (DTA) and thermogravimetric analysis (TG) were used both to characterize the samples after the complete preparation cycle and to try to follow the mechanism of phase transformations during different stages of preparation. For this purpose a Stanton-Redcroft model STA-781 instrument was used. The samples (25 to 45 mg) were contained in inconel microcrucibles, while the reference was calcined alumina powder. The measurements were made at a heating rate of 10 K min^{-1} from room temperature up to 1223 K under flowing argon gas. The apparatus was calibrated against melting temperatures of the usual standards: Zn (692.7 K), Sb

(903.5 K), NaCl (1074 K), Ag (1235 K), which spanned the temperature range of the investigation.

Results and discussion

XRD

An X-ray pattern of the sample with the nominal composition $Bi_{1.65}Pb_{0.35}Sr_2Ca_2Cu_3O_yF_{0.7}$ (Fig. 1) showed the presence of the 2212 BiSCCO in a multiphase oxide mixture already after preliminary calcination at 773 K. The only simple oxide registered in the sample was CuO. After the second heat treatment, at 1073 K for three hours, the high-T_c 2223 phase appeared. A single phase 2223 pattern was observed after 48 h sintering at 1113 K with one intermediate pulverizing and repelletizing. For comparison, in an undoped sample simple oxides SrO and CaO were observed along with CuO even after the second heat treatment (1073 K), and traces of the 2212 phase still remained in the sample after 120 h sintering at 1113 K (Fig. 2). On the surface of this pellet X-ray peaks at 19.00° and 39.33° characteristic of $Bi_2Sr_2O_5$ [15] were observed as well as the 5.78° reflection of the 2212 compound [16]. Additional heat treatment of the fluorinated sample at

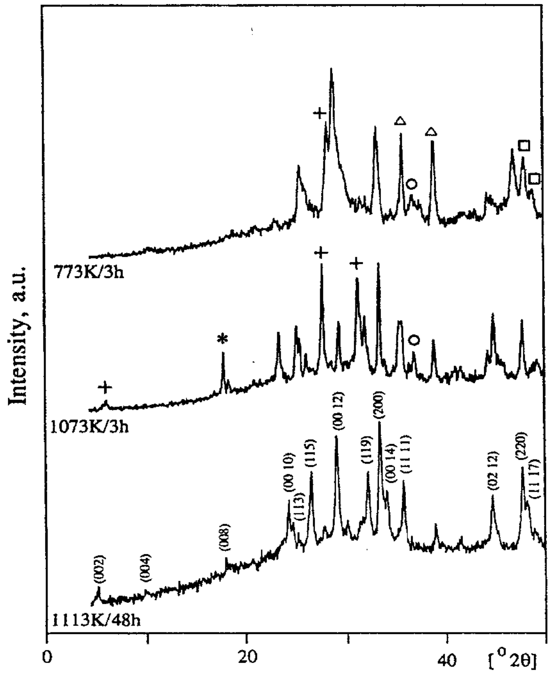

Fig. 1 XRD patterns of the Bi(Pb)SCCO 2223 sample with 0.7 at. F mol^{-1} (nominal) precalcined at 773 and 1073 K and sintered at 1113 K. (□) $Bi_2Sr_2CuO_6$; (+) 2212; (△) CuO; (o) Ca_2CuO_3; (∗) Ca_2PbO_4; (×) (Sr,Ca)O

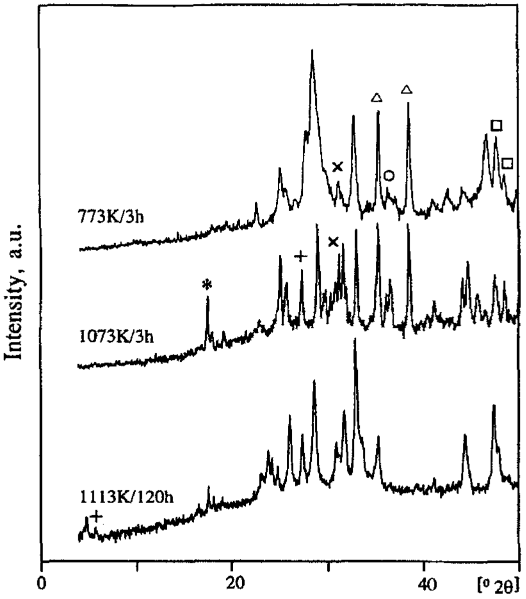

Fig. 2 XRD patterns of the pure Bi(Pb)SCCO 2223 sample precalcined at 773 and 1073 K and sintered at 1113 K. (□) $Bi_2Sr_2CuO_6$; (+) 2212; (△) CuO; (o) Ca_2CuO_3; (∗) Ca_2PbO_4; (×) (Sr,Ca)O

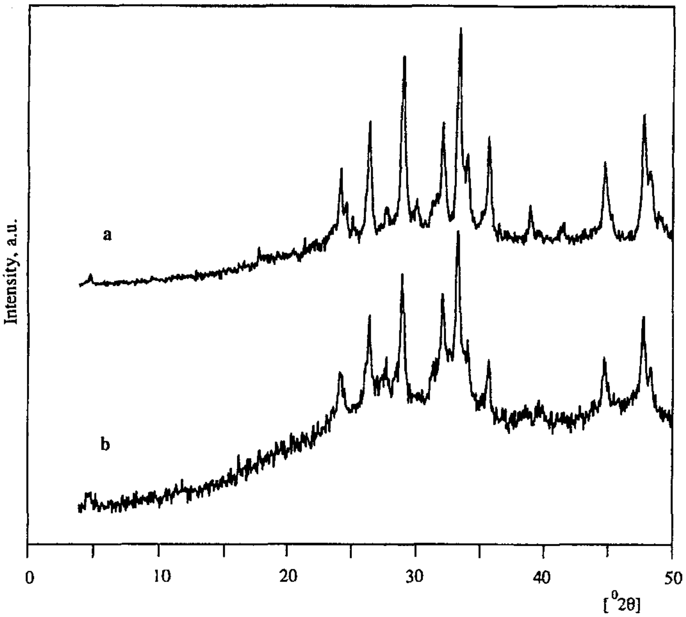

Fig. 3 XRD patterns of the Bi(Pb)SCCO 2223 sample with 0.7 at. F mol^{-1} (nominal) sintered at 1113 K (a) and ClF_3 treated at 473 K/80 Torr (b)

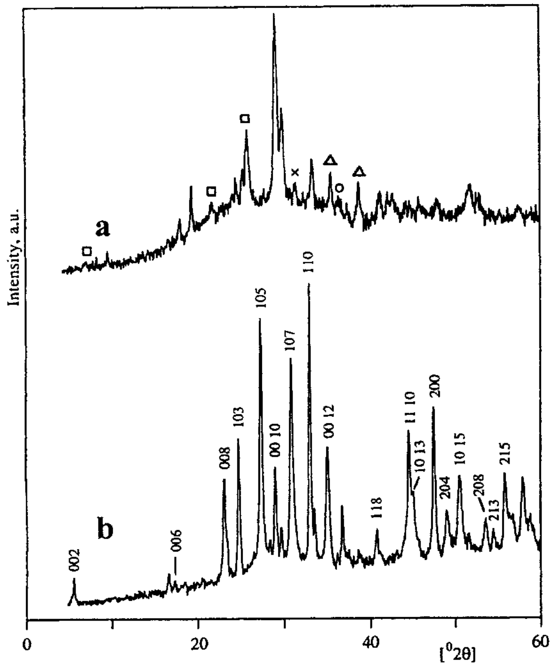

Fig. 4 XRD patterns of the Bi(Pb)SCCO 2212 sample precalcined at 773 K (a) and sintered at 1113 K (b). (□) $Bi_2Sr_2CuO_6$; (+) 2212; (△) CuO; (o) Ca_2CuO_3; (∗) Ca_2PbO_4; (×) (Sr,Ca)O

1113 K or increase of the sintering temperature resulted in partial disintegration of the 2223 phase. No significant change in the X-ray pattern was observed when up to three F atoms substituted for oxygen in the 2223 phase (Fig. 3) suggesting that the anionic radii of the oxide and fluoride ions were too close to influence noticeably the XRD pattern of this phase. For the sample with the initial composition $Bi_2Sr_2CaCu_2O_y$ some of the reflections of the 2212 phase appeared in the X-ray pattern even after precalcination at 773 K for three hours. An X-ray pure 2212 phase was obtained already after 48 h baking of the pellet at 1113 K with one intermediate regrinding (Fig. 4).

Atomic absorption

Atomic absorption of the sample with the XRD pattern shown in Fig. 1 (48 h treatment at 1113 K) gave the cation ratio Bi:Pb:Sr:Ca:Cu=1.61:0.30:1.97: 1.90:3.00 which is believed to correspond to the initial composition within the experimental limits of the analytical method estimated from the measurements of the blank with the same cation composition prepared by dissolving of the corresponding nitrates.

Potentiometric determination of fluorine

Potentiometric determination of fluorine with the standard fluoride selective electrode showed that the sintered pellet contained only a fraction (up to 10%) of fluorine initially introduced (Table 1). The main part of fluorine vaporized, presumably as HF, at the preliminary stages of preparation, prior to sintering of the pellet (sample #3 in Table 1), since the cation composition of the sample remained essentially unchanged. ClF_3 fluorination of the sample with the X-ray pattern shown in Fig. 1 at 423 K and 80 Torr for 60 min resulted in introduction of one fluorine atom into the 2223 compound (Table 1, sample 6). When the temperature was raised to 473 K, three F atoms substituted for oxygen in the same specimen (Table 1, sample 7). At still higher fluorination temperature (523 K) complete disintegration of the 2223 phase was observed in the XRD pattern, accompanied by a change in color of the sample from black to brown. The data in Table 1 is accurate to within 5% as estimated from the measurements of the fluorine concentration in a number of blank mixtures of the corresponding nitrates and PbF_2 made against the same NaF standards.

Table 1 Fluorine concentrations (F atoms per formula) initially introduced and measured with the fluoride selective electrode

Sample #	[F] Introduced	[F] Measured
1	0.2	0.04
2	0.4	0.02
3*	0.7	0.18
4	0.7	0.07
5	2.0	0.07
6**	0.7	0.99
7***	0.7	2.88

*After precalcination at 1073 K/3 h

**Sample #4, ClF_3 treated at 423 K

***Sample #4, ClF_3 treated at 473 K

Magnetic susceptibility

Temperature dependence of magnetic susceptibility is plotted in Fig. 5 for three samples: the initial Bi(Pb)SCCO with the XRD pattern shown in Fig. 1, and two fluorine substituted samples (6 and 7 in Table 1). All the samples demonstrated a sharp diamagnetic onset at approximately the same T_c=114 K, irrespective of the fluorine doping. A kink is observed on the curve (Fig. 5,1) for the initial sample at about 85 K suggesting a presence of the 2212 phase impurity in the sample, not registered in the XRD pattern (Fig. 1). This kink virtually disappears when three F atoms are introduced into the phase.

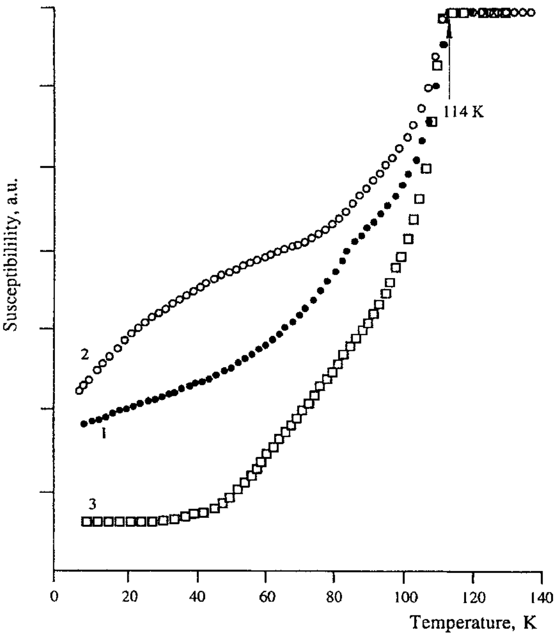

Fig. 5 Temperature dependence of magnetic susceptibility.
1 – sample with the XRD pattern shown in Fig. 3,a (#4 in Table 1); 2 – #6 in Table 1; 3 – #7 in Table 1

DTA/TG

DTA traces of the Bi(Pb)SCCO 2223 samples, both with and without fluorine in the initial mixture (Figs 6 and 7), after the preliminary stage of preparation (precalcination of the gel at 773 K for three hours), exhibited a small endothermic effect at 933 K and two pronounced peaks at higher temperatures, depending on the initial fluorine level. For pure 2223 phase with Bi:Pb=1.8:0.4 (Fig. 6) the temperatures were 1038 and 1093 K, while for a sample with two fluorine atoms per mol (nominal initial composition) the corresponding temperatures were 1018 and 1083 K (Fig. 7). It can be seen in Figs 6, 7 that the shapes of these two peaks are quite different: the first one is broad while the second is sharp. An additional small peak at 1128 K was also observed for both samples. After the second stage treatment of the powder (1073 K, 3 h) the low temperature effect disappeared in both samples, leaving the DTA curve of the doped sample with only one melting peak surrounded on both sides by shoulders (Fig. 7,b). TG curves showed considerable mass loss for both doped and undoped samples: about 12 mass% for the 773 K/3 h samples and about 3–4 mass% for the 1073 K/3 h ones. A 48 h treatment at 1113 K of the pellet with an intermediate pulverizing gave for an undoped sample a DTA scan with a single

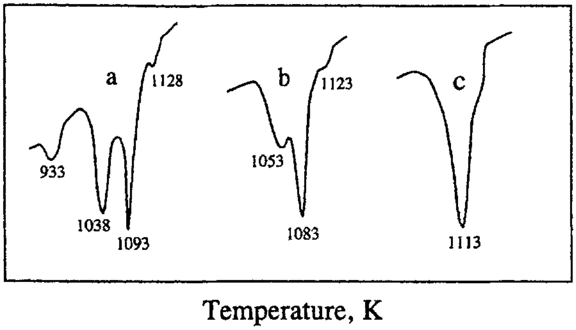

Fig. 6 DTA traces for the Bi(Pb)SCCO 2223 samples. a – precalcined at 773 K/3 h; b – precalcined at 1073 K/3 h; c – sintered at 1113 K/120 h

broad endothermic peak at 1113 K and a shoulder at a higher temperature (Fig. 6,c). The shape of the peak is characteristic of the melting of a non-stoichiometric crystalline phase. This melting temperature is gradually suppressed down to 1040 K when fluorine is introduced into the sample (Fig. 8,a–d). Also an additional small high-temperature effect is observed for the doped samples. Much the same picture is seen in Fig. 9 for the 2212 phase, with a certain shift in the temperature of the thermal effects due to compositional changes of the sample.

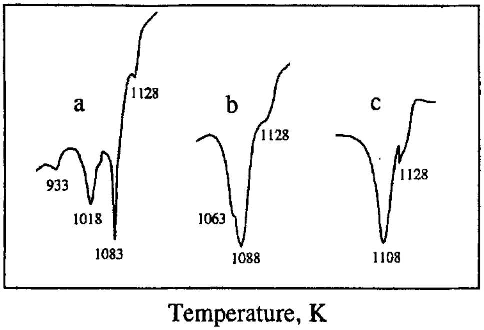

Fig. 7 DTA traces for the Bi(Pb)SCCO 2223 samples with 0.7 F mol^{-1} in the initial sample. a – precalcined at 773 K/3 h; b – precalcined at 1073 K/3 h; c – sintered at 1113 K/48 h

Thus, three endothermic peaks appeared in the DTA trace of the fluorine free BiSCCO sample after precalcination of the 2223 gel at 773 K. The corresponding temperatures are 933, 1038 and 1093 K. No thermal effects were observed at 1003 K (solid state phase transition in Bi_2O_3) meaning that pure Bi_2O_3 is not registered in the sample by DTA. This implies that mixed oxides are formed from a multicomponent gel already at the preliminary stages of the sol-gel process, even prior to calcination of the powder. Further proof of it is the endothermic peak at 933 K which, according to Majewski's [17] *T–X* phase diagram, corresponds to the formation of the 2212 phase via the phase reaction:

$$Bi_2Sr_2CuO_6+0.5Ca_2CuO_3+0.5CuO \rightarrow Bi_2Sr_2CaCu_2O_8$$

From the calorimetric data of Idemoto *et al.* [18] this reaction is indeed expected to be endothermic, with a small enthalpy change of +22 kJ mol^{-1} at 298 K. On further heating a broad endothermic peak is registered, at 1038 K for pure 2223 (Fig. 6,a) and at 1018 K for a doped sample (Fig. 7,a). It compares well with the high temperature limit of stability of $CaBi_2O_4$ reported by Roth *et al.* [19]: $CaBi_2O_4$ undergoes a peritectoid decomposition into Bi_2O_3-rich face centered cubic solid solution and $Ca_2Bi_3O_{6.5}$ at 1051 K in air while in an inert atmosphere the phase transition temperatures in this system were proved to be 15 to 30 K lower [20]. The high temperature peak corresponds to the melting of the Pb-doped 2212 phase.

Calcination of the powder at 1073 K for three hours resulted in disappearance of the low temperature peak (Figs 6,b and 7,b). Only the melting effect was registered for the fluorine doped sample, implying that fluorine accelerates con-

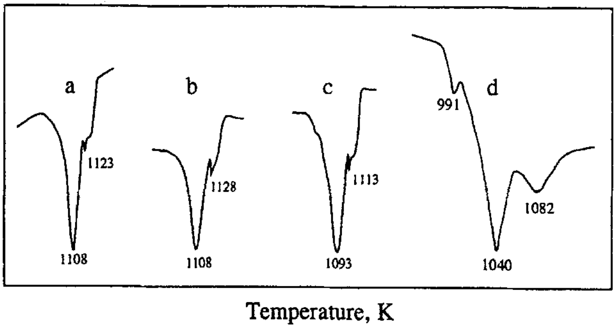

Fig. 8 DTA traces for the samples #2 (a), #4 (b), #5 (c) and #7 (d) from Table 1

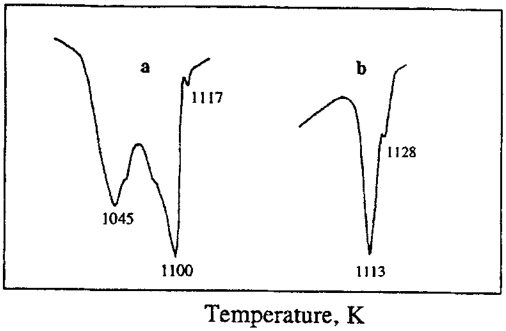

Fig. 9 DTA traces for the Bi(Pb)SCCO 2212 samples. a – precalcined at 773 K/3 h; b – sintered at 1113 K/48 h

siderably the solid state phase reactions in this system. Similar phase transformation route is observed in DTA traces of the 2212 precalcined gel (Fig. 9).

A considerable mass loss of 12% is associated with elimination of the organics from the gel, precalcined at 773 K. Calcination of the powder at 1073 K leads to complete removal of the organics and an additional mass loss of 3 to 4%. It does not originate in fluorine evolution since the mass loss is exactly the same for both pure and fluorine doped samples.

A DTA scan of the fluorine free Bi(Pb) 2223 pellet calcined for 48 h at 1113 K (Fig. 6,c) exhibits a single melting peak at 1113 K, in agreement with 1129 K for the melting of 2223 without Pb [20] (it has been shown [21] that partial substitution of Pb for Bi in 2223 led to decreasing of the phase transition temperatures). Fluorinated samples melted at somewhat lower temperatures, depending on fluorine content (Fig. 8). An additional small peak can be seen on the DTA traces which did not vanish even after repeated calcination of the pellet (72 h with intermediate pulverizing). It implies that the exact stoichiometry of both 2223 and 2212 compounds is outside the single-phase volume. Similar DTA curves were reported by Horiuchi *et al.* [9] for the fluorinated 2223 samples without Pb, obtained via solid state reaction, although these authors did not obtain a single phase 2223 sample.

Conclusion

An attempt has been made to fluorinate the Bi(Pb)SCCO 2223 compound during the sol-gel preparation and by low temperature ClF_3 treatment of the material. Up to 10% of the nominal fluorine is introduced into the sample from the fluorinated gel, while the rest of it probably evaporates as HF during the first stages of the preparation. The high-T_c phase is mainly formed at the sintering stages of the process via the phase reactions of the mixed oxides isolated from the gel during the precalcination of the powder. Reaction of the 2223 sample with 80 Torr of ClF_3 at 473 K resulted in fluorination of the material up to three F atoms per formula. At higher temperatures complete disintegration of the 2223 phase was observed.

It has been shown that fluorine in the initial mixture accelerated considerably the high-Tc phase formation in Bi–Pb–Sr–Ca–Cu–O. Although no dramatic changes in zero resistance temperature of the material were detected, this procedure can be of significant interest for the preparation of thick films and tapes with no regrinding and much shorter heat treatment time as compared to both regular solid state reaction route and even sol-gel process without fluorine.

* * *

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