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EXCESS CONDUCTIVITY ANALYSIS OF PB SUBSTITUTED Tl-1212 $(Tl_{1-x}Pb_x)Sr_2CaCu_2O_{7-\delta}$ (x = 0.1 – 0.7) PREPARED USING NANOSIZED PBO

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ABSTRACT

The effect of Pb substitution on Tl-1212 high temperature superconductors with nominal composition $(Tl_{1-x}Pb_x)Sr_2CaCu_2O_{7-\delta}$ (x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6 and 0.7) has been investigated. The samples were synthesized using the solid state reaction technique. Nano sized PbO (10 nm) was used as the starting materials for Pb. The samples were studied by powder X-ray diffraction method, electrical resistance measurements and scanning electron micrography. The resistance-temperature curves showed metallic behavior for all samples. Sample with x = 0.6 showed the highest $T_{c\ \text{onset}}$ (88 K) and $T_{c\ \text{zero}}$ (77 K). The X-ray diffraction patterns showed a single Tl-1212 phase with few weak diffraction lines of Tl-1201. The deviation of electrical resistivity from linear behavior increased with decrease in temperature due to the excess conductivity associated with Cooper pair formation. Sample with x = 0.6 has highest value of $\xi_c(0)$ = 1.3 Å which indicate lowest degree of anisotropy of Tl1212 samples.

Keywords: Superconductor; Tl-1212 phase, Pb; electrical properties

INTRODUCTION

Superconductivity in the TI-Ba-Ca-Cu-O system with T_c above 77 K was discovered by Sheng and Hermann [1]. The $Tl_2Ba_2Ca_2Cu_3O_{10-\delta}$ (Tl-2223) has the highest T_c of over 125 K [2]. The Tl-1212 was also discovered to be superconducting around 80 K. The Tl-1212 phase is difficult to prepare in pure form, because of high average Cu valence about (2.5+) [3, 4, 5]. Several factors affect the stability of the Tl-1212 crystal structure. The ionic radius of the replaced elements can be played an important role in the formation of the Tl-1212 phase [6]. Substitution can stabilize the Tl-1212 phase and its superconducting properties [7]. Partial substitution of elements Bi and Pb can stabilize the Tl-1212 superconducting phase [3, 8-10].

It is interesting to investigate the effect of Pb substitution on the superconducting characteristics of the Tl-1212 phase. In this paper we report the formation and superconducting properties of Pb substituted $(Tl_{1-x}Pb_x)Sr_2CaCu_2O_{7-\delta}$ with x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6 and 0.7. The pervious works used PbO with micrometer sized.

However, in this work we used PbO with 10 nm size as the starting material.

The two theories that describe fluctuation-induced conductivity are the Aslamazov–Larkin (AL) and Lawrence–Doniach (LD) theories [11-14]. Excess conductivity can be measured by subtracting the background normal state conductivity from the measured conductivity:
$\Delta\sigma = 1/\rho_{\text{measured}} - 1/\rho_{\text{background}}$, where ρ is the resistivity. According to the AL theory, the normalized excess conductivity $\Delta\sigma/\sigma_o$ can be calculated using a microscopic approach in the mean field region (MFR), where the fluctuations are small, and given by the relation: $\Delta\sigma/\sigma_o = A\ \varepsilon^{-\lambda}$ where σ_o is the conductivity at 300 K, ε is the reduced temperature given by the relation $\varepsilon = \ln(T/T^p_c) / T^p_c = (T - T^p_c) / T^p_c$, where T^p_c is the temperature of the peak obtained from $d\rho/dT$. A is the AL temperature independent constant and λ is the critical exponent which is related to the conduction dimensionality D where $\lambda = 2 - D/2$. For the 1-dimensional region (1D), $\lambda = 1.5$, for 2-dimensional region (2D), $\lambda = 1.0$, and for 3D, $\lambda = 0.5$. λ can be obtained from the slope of $\ln(\Delta\sigma/\sigma_o)$ versus $\ln(\varepsilon)$ plot. Interestingly, elemental substitutions also contribute to the changes in T_{2D-3D} and coherence length. For Tl-1212, this enhancement leads to a longer $\xi_c(0)$ and enhanced the superconducting properties due to the reduction in the anisotropy, γ and increase in the interlayer coupling, J .

Using the LD model, the coherence length along the *c*-axis, $\xi_c(0)$ for polycrystalline samples at the transition temperature, T_{2D-3D}, can be obtained from $T_{2D-3D} = T_c\ [1 + (2\ \xi_c(0)/d)^2]$.
where d is the distance between the superconducting layers. For Tl-1212, d = 3.18 Å. Using the LD model, the interlayer coupling, J based on Josephson coupling as a result of $\xi_c(0)$ interaction with the superconducting layers is given by $J = [2\ \xi_c(0)\ ]^2/d^2$.
For layered superconducting systems the anisotropy γ is expressed by $\gamma = \xi_{ab}(0)/\xi_c(0)$ where $\xi_{ab}(0)$ is the *ab*-coherence length which is between 10 and 20 Å for copper oxide-based HTSC. In this work $\xi_{ab}(0)$ is assumed 10 Å.

EXPERIMENTAL DETAILS

Samples with the nominal starting composition of $(Tl_{1-x}Pb_x)Sr_2CaCu_2O_{7-\delta}$ (x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6 and 0.7) were prepared by using the solid-state reaction method using metal oxides powders. Appropriate amounts of high purity (>99.99%) SrO, CaO and CuO were mixed and ground in an agate mortar. The precursor powders were ground for one hour and heated at 900 C^o in air for 24 h followed by furnace cooling to room temperature. The powders were reground and heated at 900 C^o in air for 24 h followed by furnace cooling to room temperature to obtain a uniform black powder. Appropriate amounts of Tl_2O_3 and PbO (10 nm) were added to the precursor and completely mixed. The powders were pressed into pellets with diameter of 13 mm and thickness of around 2 mm. The pellets were heated at around 1000 ºC for 4 min in flowing O_2 followed by furnace cooling.

The samples were analyzed by powder X-ray diffraction method using Bruker D8

Advance diffractometer with CuKα source. The volume fraction of Tl-1212 and Tl-1201 phase was estimated by assuming that the amounts of 1212 and 1201 phases are proportional to the strongest diffraction line of each phase, i.e (103) peak for 1212 phase and (102) peak for 1201 phase. The lattice parameter of the samples was calculated by employing at least 15 diffraction peaks.

The electrical resistance (dc) measurements were carried out using the four-point probe method with silver paint contacts. A CTI Cryogenics closed cycle refrigerator model 22 and Lake Shore temperature controller model 340 were used for temperature-dependent measurements. The $T_{c\ zero}$ is defined as the temperature where the temperature becomes zero and $T_{c\ onset}$ is defined as the temperature where there is sudden drop in the resistance. The Van der Pauw method was used to determine room-temperature resistivity.

RESULTS AND DISCUSSION

Figure 1 shows the powder X-ray diffraction patterns of $(Tl_{1-x}\ Pb_x)Sr_2CaCu_2O_{7-\delta}$ for (x = 0.1, 0.4 and 0.6). The patterns indicated a single Tl-1212 phase with tetragonal unit cell (space group, P4/mmm) with few weak diffraction lines of Tl-1201, and an unknown phase. The lattice parameters for x = 0.1 sample were a = 3.7907 Å and c = 12.0595 Å and lattice parameters for 0.4 sample were, a = 3.7906 Å and c = 12.0618 Å while lattice parameters for 0.6 sample were, a = 3.7911 Å and c = 12.0620 Å.

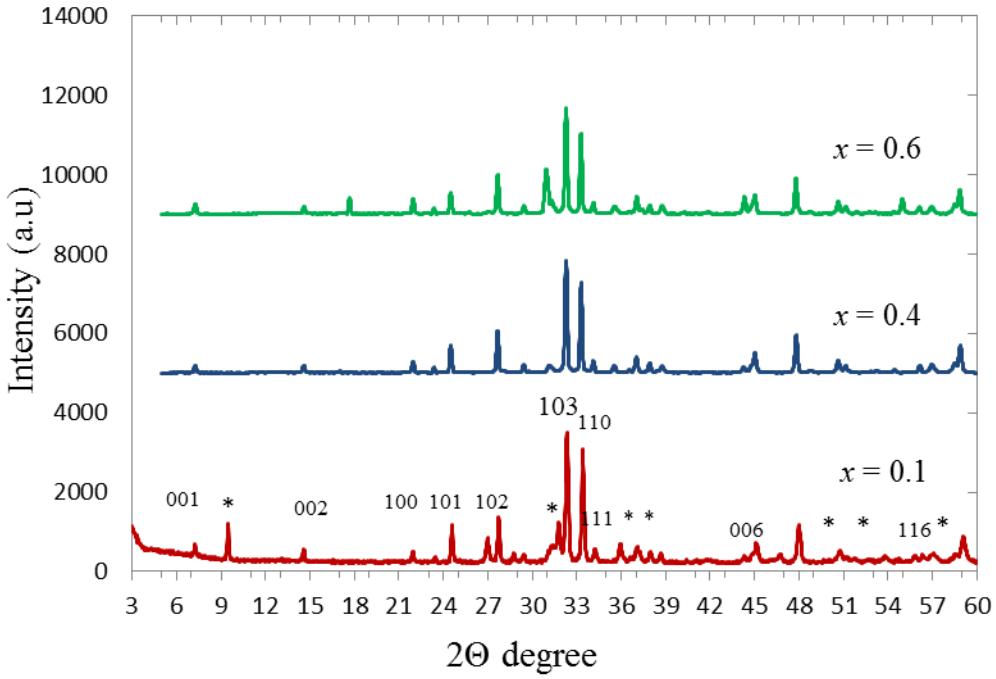

Figure 1: Powder X-ray diffraction patterns for $(Tl_{1-x}\ Pb_x)Sr_2CaCu_2O_{7-\delta}$ x = 0.1, 0.4 and 0.6. (*) indicates the Tl-1201 phase

Figure 2 shows the electrical resistance versus temperature curves of the $(Tl_{1-x}Pb_x)Sr_2CaCu_2O_{7-\delta}$ for x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6 and 0. All samples showed metallic normal-state behavior. Sample with x = 0.6 showed the highest $T_{c\ \text{onset}}$ 88 K and $T_{c\ \text{zero}}$ 77 K (Figure 3). The normal state electrical resistance increased with increased of Pb content. Figure 2 shows $T_{c\ \text{onset}}$, $T_{c\ \text{zero}}$ as a function of x. $T_{c\ \text{onset}}$ increased for $x \leq 0.6$ and decreased for $x > 0.6$. $T_{c\ \text{onset}}$ for the samples with x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6 and 0.7 was observed at 37, 47, 71, 79, 87, 88 and 87 K, respectively. The highest $T_{c\ \text{onset}}$ was observed at x = 0.6 indicating an optimal doping level. This also coincided with the lowest normal state resistivity (at 300 K), which indicated that for Tl-1212 compounds existence of maximum T_c usually indicates optimization of hole concentration as a result of substitution. It is generally known that the optimum valency of Cu in the 1212 phase is between 2.2+ and 2.3+.This shows that in our samples the valence state of Pb at the Tl site is 4+. Pb^{4+} is able to occupy the thallium layers because of its smaller size compared to Tl^{3+}, due to the Jahn Teller nature of Cu which allows a high flexibility of the Cu-O apical distance making it possible for Pb with very high valency to occupy the Tl^{3+} site.

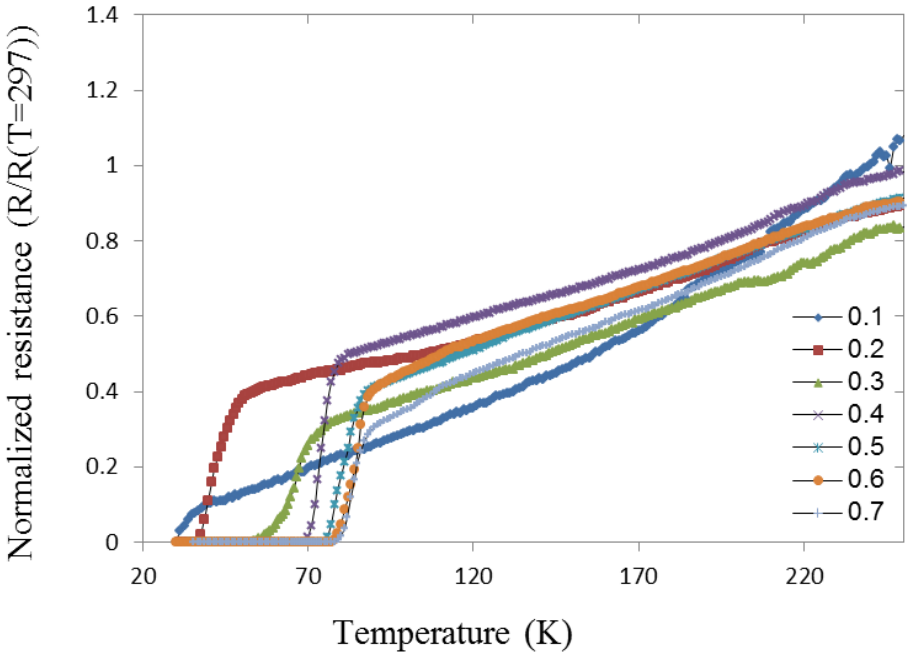

Figure 2: The temperature dependence of the resistance of $(Tl_{1-x}Pb_x)\ Sr_2CaCu_2\ O_{7-\delta}$ for x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6 and 0.7

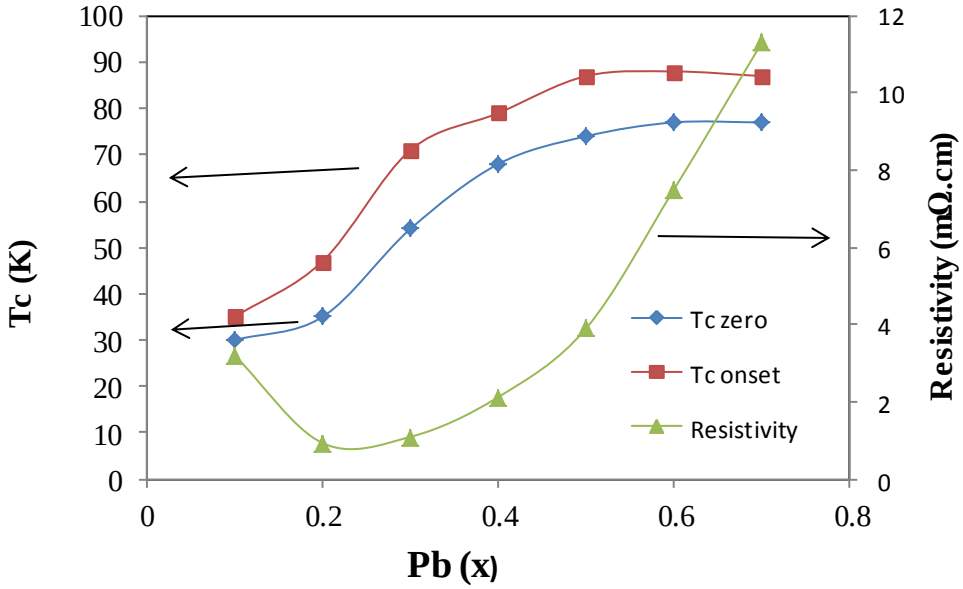

Figure 3: Normal state electrical resistivity at 300 K and the variation of $T_{c\ onset}$ and $T_{c\ zero}$ as function of $(Tl_{1-x}Pb_x)Sr_2CaCu_2O_{7-\delta}$

Figure 4 (a) shows the electrical resistivity dependence of temperature together with linear fitting of normal state with $\rho = \alpha + \beta T$ for x = 0.4 - 0.7. The linear fits for the data at high temperatures are shown as straight lines. The deviation from linear behavior increases with the temperature decreasing because excess conductivity that associated with Cooper pair formation. Figure 4(a) also shows the derivative of the resistivity against temperature. The peak temperature T^p_c was used to calculate the reduced temperature ε, where $\varepsilon = \ln(T/T^p_c)/T^p_c$. The samples with x = 0.4, 0.7 have single peak while sample with x = 0.5 has double peaks transition. On the other hand sample with x = 0.6 has sharp peak at 64 K with small hump at 80 K.

For the analysis of excess conductivity expected as the temperature decreased, *ln* $(\Delta\sigma/\sigma)$ versus *ln* ε was plotted in the range of $-4.5 < ln\ \varepsilon < -0.3$ for samples with x = 0.4-0.7 (Figure 4 (b). The samples with x = 0.4 - 0.7 exhibited a transition from 2D to 3D behavior.

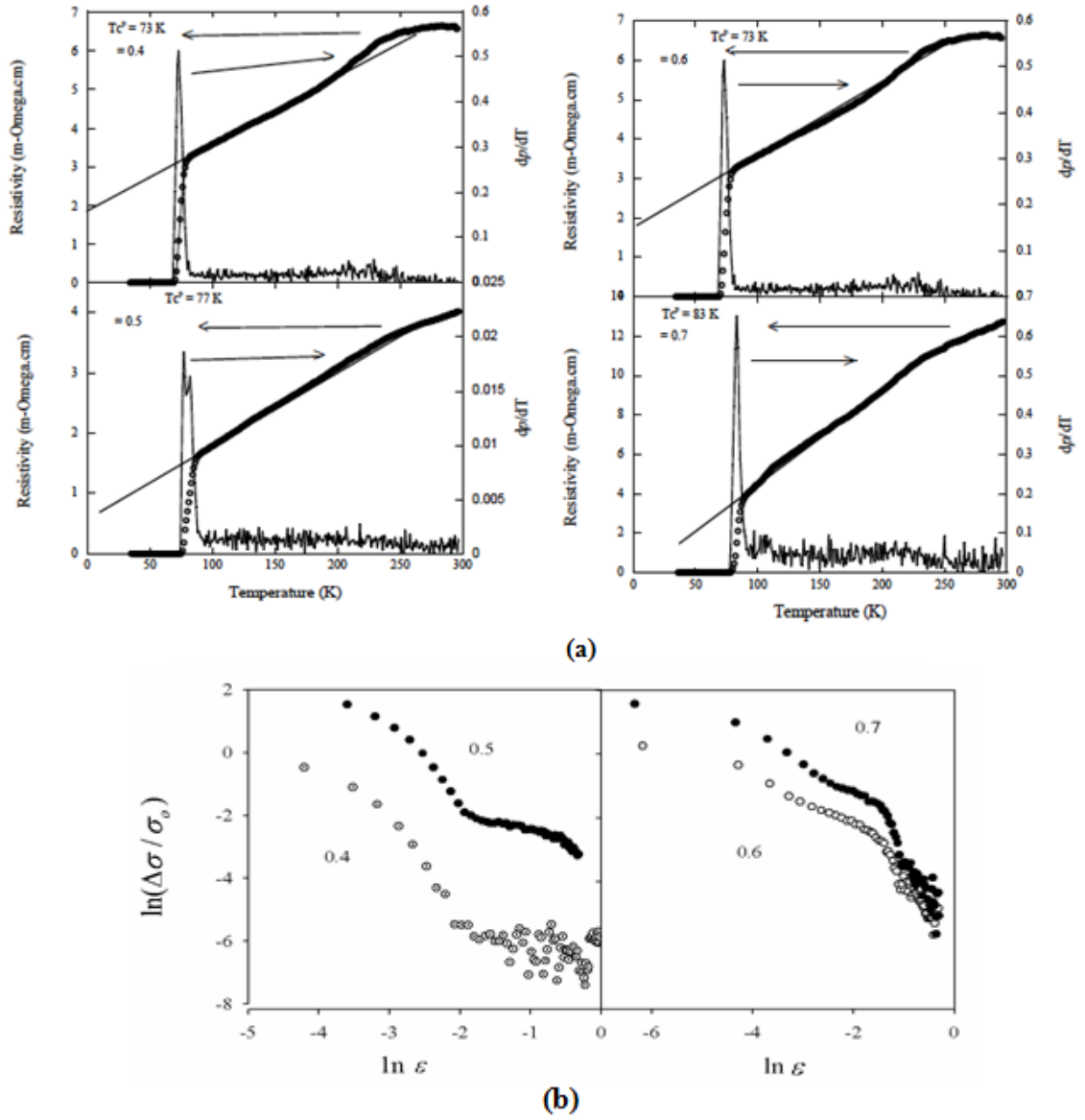

Figure 4: (a) Electrical resistivity vs. temperature plot with extrapolated linear fit and (dρ /d*T*), residual resistivity ρ_o and (b) the ln ($\Delta\sigma/\sigma_o$) versus *ln* (ε) plot with the exponent (λ_2 and λ_3) values gives the excess conductivity behaviour of $(Tl_{1-x}Pb_x)Sr_2CaCu_2O_{7-\delta}$ with x = 0.4, 0.5, 0.6 and 0.7

The highest $T_{c\ zero}$ was observed for sample with x = 0.6 and 0.7. The doping with Pb may result in increase of hole concentration that result in increase of $T_{c\ zero}$ with increase Pb contents. It also results in transition from 2 to 3D behavior before the material become in superconducting state. The average slope β increased from 3×10^{-3} to 430×10^{-3} (mΩ.cm)/K with increase of x from 0.4 to 0.7. The values of $\xi_c(0)$ ranged from 0.61 to 1.3 Å. Sample with x = 0.6 has highest value of $\xi_c(0)$ = 1.3 Å which indicate lowest degree of anisotropy. The scanning electron microscopic (SEM) images of x = 0.1 and 0.4) are shown in Figure 5. There is no noticeable change in the grain

morphology with different Pb concentrations.

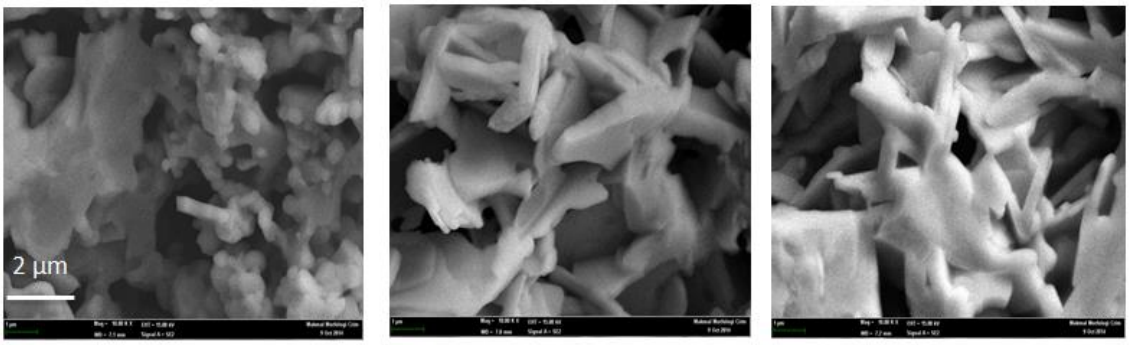

Figure 5. Scanning electron micrographs (at 15Kv) for $(Tl_{1-x}Pb_x)Sr_2CaCu_2O_{7-\delta}$ for (a) x = 0.1, (b) x = 0.4 and (c) x = 0.6

CONCLUSIONS

In conclusion, the effects of elemental substitutions on samples with nominal starting composition $(Tl_{1-x}Pb_x)Sr_2CaCu_2O_{7-\delta}$ have been studied by dc resistivity and X-ray powder diffraction method. The resistance-temperature curves showed metallic behavior for all samples. The X-ray diffraction patterns showed single Tl-1212 phase with tetragonal unit cell (space group, P4/mmm) with few weak diffraction lines of Tl-1201, and an unknown phase. Fluctuation induced conductivity of the samples with x = 0.4, 0.7 showed single peak while sample with x = 0.5 has double peaks transition. On the other hand, sample with x = 0.6 has sharp peak at 64 K with small hump at 80 K.

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