Coexistence of electrons and holes in $BaBi_{0.25}Pb_{0.75}O_{3-\delta}$ detected by thermoelectric-power measurements

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Seebeck coefficients of $BaBi_{0.25}Pb_{0.75}O_{3-\delta}$ ($0.00 \le \delta \le 0.08$) were measured as a function of temperature up to 1100 K in various O_2 partial pressures. The Seebeck coefficient of $BaBi_{0.25}Pb_{0.75}O_{3.00}$ below 300 K was negative by a few $\mu V/K$ and showed linear temperature dependence, indicating a metallic or semimetallic nature of the carrier electrons. Above 300 K, the Seebeck coefficient ($\delta = 0.00$) increased, becoming positive around 400 K. Curve fitting with an assumption of the coexistence of electrons that show delocalized character and holes that have a localized nature was carried out to determine the relationship between the Seebeck coefficients and the temperature of the sample. The temperature dependence of not only the Seebeck coefficient but also the electrical conductivity of the sample could be well explained by the assumption described above. From the comparison with electronic-band calculations, it is deduced that electrons with high mobility and holes with low mobility are the product of delocalized bands composed of Pb(Bi) 6*s* and O 2*p* antibonding orbitals and localized bands composed of O 2*p* isolated orbitals, respectively. The Seebeck coefficients of the samples with δ values of 0.025–0.08 were also slightly negative at low temperatures and had values of $\sim 20\ \mu V/K$ at around 1100 K. Finally, it could also be deduced that electrons and holes existed simultaneously in samples with an oxygen deficiency.

I. INTRODUCTION

Since the discovery of superconductivity in $BaBi_{0.3}Pb_{0.7}O_3$ at 13 K,[1] many papers have been published to elucidate the conduction mechanism of $BaBi_{1-x}Pb_xO_3$. However, there have been contradictions in the literature as to whether the major carrier in this system is holes or electrons. Thanh, Koma, and Tanaka[2] prepared high-density ceramic samples and reported that $BaBi_{1-x}Pb_xO_3$ showed a semiconductive temperature dependence of resistivity for $0.55 \le x < 0.7$ and a metallic temperature dependence of resistivity for $0.7 \le x \le 1.0$. Superconductivity was observed for the composition region $0.65 \le x \le 0.9$. Hall measurements were also performed on the samples, and it was concluded that electrons were the major carrier in the compositional range at which superconductivity appeared. Recently, Suzuki prepared $BaBi_{1-x}Pb_xO_3$ thin films by sputtering and reported negative Hall coefficients in the range of $0.7 \le x \le 1.0$.[3,4] The measurement of Seebeck coefficients at temperatures ranging from 4.2 K to room temperature supported the existence of electron carriers in the range $0.7 \le x \le 1.0$.[5] Conversely, measurements of the thermoelectric power at temperatures above 973 K detected hole-type conduction in this system. Yamauchi, Idemoto, and Fueki measured positive Seebeck coefficients in this system in this temperature range. They also measured a dependence of electrical conductivity on oxygen partial pressure at high temperatures, and concluded that holes were the conduction carrier of this system.[6]

We deduced that one of the reasons for the abovementioned contradictions was the absence of research on the temperature dependence of electrical conductivity and the values of Seebeck coefficients, for a wide range of temperatures, with consideration of oxygen deficiency. In this study, electrical conductivities and Seebeck coefficients of $BaBi_{0.25}Pb_{0.75}O_{3-\delta}$ in various O_2 partial pressures were measured in the temperature range from 10 to 1100 K to clarify the conduction carriers. Curve fitting was carried out to analyze the temperature dependence of electrical conductivity and the values of Seebeck coefficients of $BaBi_{0.25}Pb_{0.75}O_{3.00}$, assuming the coexistence of electrons and holes, which showed high mobility and low mobility, respectively. The fitting suggested that the above assumption was suitable to explain the conduction mechanism of $BaBi_{0.25}Pb_{0.75}O_{3.00}$. The correspondence between this assumption and the results of electronic-band calculations of $BaBi_{1-x}Pb_xO_{3.00}$, which suggest that part of the electron carriers was generated by energy overlapping of Pb(Bi) 6*s* orbitals and isolated O 2*p* orbital,[7,8] was also examined. The effect of oxygen deficiency (δ) on the character of conduction carriers was studied as well.

II. EXPERIMENTAL

A. Sample preparation

$BaBi_{0.25}Pb_{0.75}O_{3.00}$ ceramic samples were prepared from powdered $BaCO_3$ (99.9%), Bi_2O_3 (99.9%), and Pb_3O_4 (99.9%). The prescribed amounts of oxides and carbonates were mixed in ethanol in an agate mortar and dried at 50 °C. The mixtures were heated at 720 °C for 12 h in the O_2 atmosphere. The calcined samples were ground, pressed into pellets, and heated at 800 °C for 16 h in the O_2 atmosphere. The sintered pellets were further heated at 850 °C for 12 h in a N_2 atmosphere to obtain samples with a high density (more than 85%), followed by annealing at 800 °C for 60 h in the O_2 atmosphere. The oxygen content of the samples was confirmed to be 3.00±0.01 by iodometric titration (the method was described in detail in a previous paper).[9] No diffraction peak assigned to an impurity was detected in the x-ray-diffraction patterns. The specimens with δ of 0.025 and 0.08 were prepared by annealing the $BaBi_{0.25}Pb_{0.75}O_{3.00}$ sample at the temperature and O_2 partial pressure determined by thermogravimetry (TG) data, followed by quenching.[10]

B. Measurement of electrical conductivity

Electrical conductivity of $BaBi_{0.25}Pb_{0.75}O_{3-\delta}$ was measured by a four-probe method. The measurement temperature ranged from 4.2 to 1100 K. Gold wires (ϕ=0.3 mm) were employed as electrodes to avoid chemical reactions between the sample and the electrode at high temperatures. Below room temperature, the conductivities of samples with various δ, prepared by the method described in Sec. II A, were measured, since variation of δ was not probable at low temperature. At high temperatures, measurements of equilibrium-state electrical conductivities were carried out under various O_2 partial pressures. Relationships among the electrical conductivity, temperature, and δ were calculated by using the results of this experiment and the TG data.[10]

C. Measurement of Seebeck coefficient

Seebeck coefficients of $BaBi_{0.25}Pb_{0.75}O_{3-\delta}$ were measured at temperatures ranging from 10 to 1100 K in various O_2 partial pressures. At the low-temperature range of 10 K–room temperature, specimens with various δ prepared by the method described in Sec. II A were used for the measurement, since δ should be constant during the measurement at this temperature range. A temperature difference between the electrodes as large as ~3 K (ΔT) was applied by heating one side of the sample in cryostats by irradiation with light from a small lamp. The thermoelectric power (ΔV) was measured as a function of ΔT (more than ten data points). After confirming the linearity of ΔV vs ΔT, the Seebeck coefficient was calculated. Copper wires (ϕ0.07 mm) were used as the electrode and the lead. In the temperature range from room temperature to 1100 K, ΔT (as large as ~3 K) was introduced by heating one side of the sample with a subheater. ΔV was plotted as a function of more than ten values of ΔT. From the slope of ΔV vs ΔT, the Seebeck coefficient was calculated. To clarify the relationship among the Seebeck coefficient, temperature, and δ, measurements were carried out under various O_2 partial pressures. The values of δ during the measurement were estimated using TG data.[10] Gold wires (ϕ0.3 mm) and platinum lines (ϕ0.5 mm) were used as the electrode and the lead, respectively. Experimentally obtained Seebeck coefficients were calibrated by the reported absolute Seebeck coefficients of copper[11] and platinum.[12]

III. RESULTS

As described in Sec. I, there have been contradictions concerning the type of carriers in $BaBi_{0.25}Pb_{0.75}O_{3.00}$. Hall measurements and Seebeck measurements at low temperatures indicated electrons as the major carrier, whereas Seebeck measurements at high temperatures suggested holes as the predominant carrier. One of the causes of the contradictions is that oxygen deficiency (δ), that should be generated during the measurement, has not been considered. The authors measured the amount of oxygen deficiency at various temperatures and O_2 partial pressures by TG.[10] By using the TG data, the electrical conductivity and Seebeck coefficient at high temperatures were calculated as a function of δ.

Figure 1 shows the temperature dependence of the resistivity of $BaBi_{0.25}Pb_{0.75}O_{3-\delta}$ in the temperature range from 4.2 to 1100 K. Oxygen deficiency (δ) was expressed as a parameter in the figure. A sharp drop of resistivity, ascribed to the superconducting transition, was observed at 13 K on the specimen whose δ was 0.00. Also observed was almost constant resistivity (on the order of 10^{-3} Ω cm) in the measured temperature range above 13 K, which suggested that the behavior of the conduction carrier was not perfectly metallic. Upon increasing δ from 0.00 to 0.08, resistivity increased and the temperature dependence of resistivity became semiconductive. The superconducting transition disappeared above 4 K for the specimen with δ of 0.08.

Figure 2 shows the dependence of Seebeck coefficient of $BaBi_{0.25}Pb_{0.75}O_{3-\delta}$ on oxygen partial pressure at high temperatures. From the data of Fig. 2 and those of TG,[10] the relationships among the Seebeck coefficient temperature, and δ were calculated. Figure 3 shows the calculated relationships between temperature and Seebeck coefficient of $BaBi_{0.25}Pb_{0.75}O_{3-\delta}$ in the temperature range from 10 to 1100 K. Below 200 K, the Seebeck

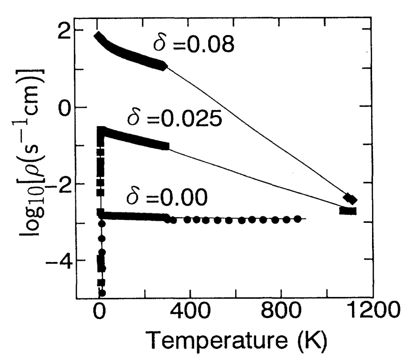

FIG. 1. Temperature dependence of electrical resistivity of $BaBi_{0.25}Pb_{0.75}O_{3-\delta}$. δ during the measurement at high temperatures was estimated by TG data (Ref. 10). Below room temperature, specimens with various δ were used for the measurement.

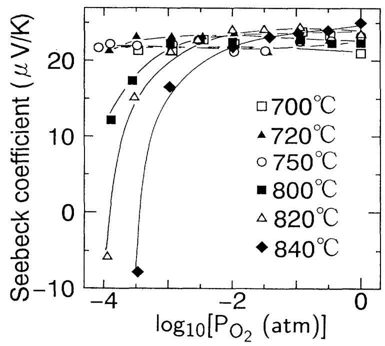

FIG. 2. Variation of the equilibrium-state Seebeck coefficient of $BaBi_{0.25}Pb_{0.75}O_{3-\delta}$ as a function of O_2 partial pressures at high temperatures.

coefficient of $BaBi_{0.25}Pb_{0.75}O_{3.00}$ had a negative value of a few microvolts and almost linear relationship against temperature, which suggested metallic or semimetallic character of the electrons. This result agreed well (within the experimental error) with the data reported by Tani, Itoh, and Tanaka at low temperatures, which are also depicted in Fig. 3.[5] The value of the Seebeck coefficient increased above 200 K, changed to a positive value around 400 K and reached a value of $\sim 20\ \mu V/K$ around 873 K, suggesting a semiconducting nature of the holes[13] at high temperatures. In the oxygen-deficient specimens, also observed were negative values at low temperatures and positive values at high temperatures.

IV. DISCUSSION

First, we discuss the temperature dependence of the Seebeck coefficient and electrical conductivity of the specimen without oxygen deficiency ($BaBi_{0.25}Pb_{0.75}O_{3.00}$). The Seebeck coefficient takes negative and positive values at low temperatures and high temperatures, respectively, as shown in Fig. 3. This may be the cause of the conflict in the literature on the type of carriers in $BaBi_{0.25}Pb_{0.75}O_{3.00}$. Since oxygen deficiency was not observed in the O_2 atmosphere and in the temperature range from 10 to 873 K by thermogravimetry,[10] the change of sign of the Seebeck coefficient could not be attributed to oxygen deficiency. Thus, coexistence of electrons and holes in $BaBi_{0.25}Pb_{0.75}O_{3.00}$ was suggested. Further suggested from Fig. 3 was a metallic or semimetallic character of the electrons and a semiconducting character of the holes. Curve fitting for the temperature dependence of the Seebeck coefficient and electrical conductivity was examined in the following, which is a modification of the method applied to analyze the temperature dependence of the Seebeck coefficient of $Tl_2Ba_2Ca_2Cu_3O_{10-\delta}$ by Xin and co-workers.[14]

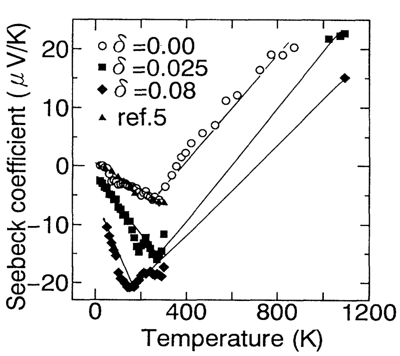

FIG. 3. Seebeck coefficient vs temperature of $BaBi_{0.25}Pb_{0.75}O_{3-\delta}$. At higher temperatures than room temperature, δ during the measurement was estimated from the TG data (Ref. 10). The data for samples with various δ were employed below room temperature. The data from Ref. 5 are also plotted for comparison.

For the case of coexisting electrons and holes, the Seebeck coefficient Q can be described by

$$Q=(Q^+\sigma^+ + Q^-\sigma^-)/\sigma \ , \tag{1}$$

where $\sigma=\sigma^+ + \sigma^-$ is the sum of the electrical conductivities by holes (σ^+) and by electrons (σ^-) and Q^+ and Q^- are Seebeck coefficients due to holes and electrons, respectively. In the case when the electron conduction is metallic or semimetallic, Q^- is described as follows:

$$Q^- = -(\pi^2/3)(k^2T/e)\{1/(E_F-E_C)\} \ , \tag{2}$$

where k, T, and e are the Boltzmann constant, temperature, and elemental electronic charge, respectively. E_F is the Fermi energy and E_C is the energy at the bottom of the conduction band.

As to σ^-, two kinds of equations were employed for the fitting. Since the observed temperature dependence of σ is constant as Fig. 2 shows, constant (i.e., temperature-independent) σ^- can be assumed as follows:

$$\sigma^- = A \ , \tag{3a}$$

where A is a constant. When metallic electrical conductivity was assumed, the following equation could be applied instead of Eq. (3a):

$$\sigma^- = A/T \ . \tag{3b}$$

If the holes are localized, Q^+ and σ^+ can be expressed as follows:

$$Q^+ = (k/e)(\Delta E_h/kT + B) \ , \tag{4}$$

where ΔE_h and B are the activation energy for the generation of holes and a constant, respectively, and

$$\sigma^+ = C\exp(-\Delta E_h/kT) \ , \tag{5}$$

where C is a constant. Assuming that $\sigma^- \gg \sigma^+$, the following two equations can be satisfied:

$$\sigma^-/\sigma \approx 1 \ , \tag{6}$$

and, if Eq. (3a) is applicable,

$$\sigma^+/\sigma = (C/A)\exp(-\Delta E_h/kT) \tag{7a}$$

or if Eq. (3b) is applicable

$$\sigma^+/\sigma = (CT/A)\exp(-\Delta E_h/kT) \ . \tag{7b}$$

By substitution of Eqs. (2), (4), (6), and (7a) or (7b) into

Eq. (1), we can obtain the following two equations. One is applicable if σ is temperature independent [Eq. (3a)],

$$Q=\alpha T+(\beta\Delta E_h/kT+\gamma)\exp(-\Delta E_h/kT) . \quad (8a)$$

The other one is the equation applicable assuming metallic conductivity for σ^-:

$$Q=\alpha T+(\beta\Delta E_h/k+\gamma T)\exp(-\Delta E_h/kT) , \quad (8b)$$

where

$$\alpha=-(\pi^2/3)(k^2/e)\{1/(E_F-E_C)\} , \quad (9)$$

$$\beta=Ck/Ae , \quad (10)$$

and

$$\gamma=BCk/Ae . \quad (11)$$

Also, σ can be expressed as follows by using Eqs. (3a) or (3b) and (5):

$$\sigma=A+A(\beta e/k)\exp(-\Delta E_h/kT) , \quad (12a)$$

when Eq. (3a) holds and

$$\sigma=A/T+A(\beta e/k)\exp(-\Delta E_h/kT) \quad (12b)$$

when Eq. (3b) holds.

Figure 4 shows the least-fitting curve for the temperature dependence of the Seebeck coefficient of $BaBi_{0.25}Pb_{0.75}O_{3.00}$ by using Eq. (8a) with the least-squares method. The fitted curve reproduces the observed one. The parameters for the best fit were $\alpha=-3.13\times10^{-2}$ $\mu V/K^2$, $\beta=3.92\times10$ $\mu V/K^2$, $\gamma=1.27\times10^2$ $\mu V/K^2$, and $\Delta E_h=98$ meV. E_F-E_C calculated from α using Eq. (9) was 0.78 eV. Mattheiss and Hamann reported a calculation of the electronic-band structure of $BaBi_{0.3}Pb_{0.7}O_3$ by the linearized-augmented-plane-wave (LAPW) method.[7,8] Their calculation shows that the Fermi level, which exists in the conduction band composed mainly of Pb(Bi) 6s orbitals, is located ~1.8 eV above the bottom of the conduction band. Considering the accuracy of the band calculation, our experimentally obtained E_F-E_C of 0.78 eV showed semiquantitative agreement with the value obtained by their calculation. Curve fitting for the relationship between temperature and electrical conductivity was also examined using Eq. (12a). The above-described values of β and ΔE_h were employed for the fitting. Figure 5 shows the fitting results on the assumption that $A=680$ S cm^{-1}. Fairly good agreement was observed between calculation and experiment.

Figures 4 and 5 also show the results of curve fitting using Eqs. (8b) and (12b) assuming perfect metallic behavior of the electrons. The experimental value of the temperature dependence of the Seebeck coefficient agreed well with the calculated one. Parameters for the fitting are as follows: $\alpha=-2.82\times10^{-2}$ $\mu V/K^2$, $\beta=2.47\times10^{-1}$ $\mu V/K^2$, $\gamma=-1.37\times10^{-1}$ $\mu V/K^2$, and $\Delta E_h=98$ meV. However, the dependence of electrical conductivity on temperature did not agree with the calculated one, suggesting that the behavior of electrons is not perfectly metallic, i.e., scattering mechanisms other than the one originating from phonons in $BaBi_{0.25}Pb_{0.75}O_{3.00}$ exist.

Thus, coexistence of high-mobility electrons and low-mobility holes in $BaBi_{0.25}Pb_{0.75}O_{3.00}$ was suggested in our experiment. Mattheiss and Hamann carried out electronic-band calculations of $BaBi_{1-x}Pb_xO_3$ and attributed the generation of mobile electrons in $BaPbO_3$ to overlapping between the band composed of mainly Pb 6s orbitals and that of mainly O 2p orbitals. In other words, the following equilibrium state is satisfied:

$$Pb^{4+}+O^{2-}\leftrightarrow Pb^{3+}+O^- .$$

In this formula, Pb^{3+} and O^- mean that electrons exist on Pb 6s orbitals and holes exist on O 2p isolated orbitals. The dispersion of the former is large while that of the latter is small. Therefore generation of electron carriers with high mobility in $BaPbO_3$ inevitably involves generation of holes with low mobility. Following the electronic-band calculation, band overlap between bands composed of mainly Pb(Bi) 6s orbitals and those of mainly O 2p isolated orbitals was also observed in the electronic structure of $BaBi_{0.3}Pb_{0.7}O_3$. This suggests the coexistence of high-mobility electrons and low-mobility holes in this

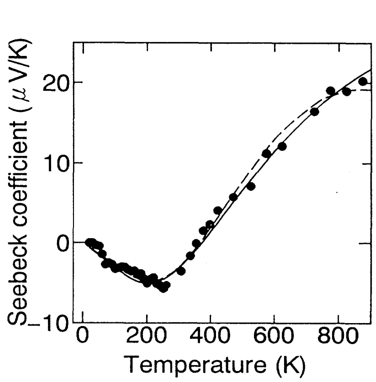

FIG. 4. Curve fitting of the temperature dependence of the Seebeck coefficient of $BaBi_{0.25}Pb_{0.75}O_{3.00}$. Measured Seebeck coefficients are expressed by closed circles. Solid and dashed lines represent curves calculated by using Eqs. (8a) and (8b), respectively. See text for parameters employed.

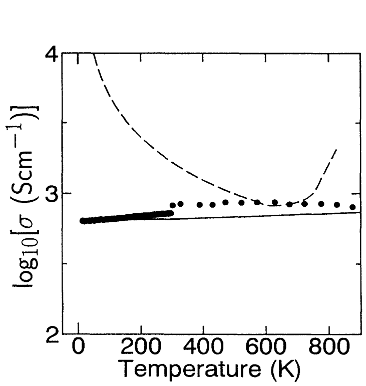

FIG. 5. Curve fitting of the dependence of electrical conductivity on the temperature of $BaBi_{0.25}Pb_{0.75}O_{3.00}$. Experimental data are expressed by closed circles. Solid and dashed lines represent curves calculated by using Eqs. (12a) and (12b), respectively. The parameters are described in the text.

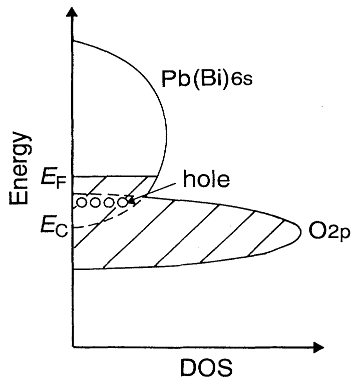

FIG. 6. Schematic electronic-band diagram of $BaBi_{0.25}Pb_{0.75}O_{3.00}$ proposed in this study. Electrons fill the hatched conduction band mainly composed of Pb(Bi) 6*s* orbitals and holes exist on bands composed of isolated O 2*p* orbitals. $E_F - E_C = 0.78$ eV and the activation energy for generation of holes (ΔE_h) is 98 meV.

system as shown in Fig. 6, which agrees well with our Seebeck and electrical conductivity measurements.

For the specimens with oxygen deficiency, the above curve fitting was not successfully applied due to the lack of data between 300 and 1023 K. This was because it was experimentally difficult to measure the electrical conductivity and Seebeck coefficient keeping δ constant in this temperature range. However, it was suggested that coexistence of electrons and holes also occurred in the oxygen-deficient specimens, since they showed a negative value of the Seebeck coefficient at low temperature and a positive value at high temperature. Larger negative absolute values of the Seebeck coefficient of the specimens with oxygen deficiency at low temperature than that of the specimen without oxygen deficiency suggest that under oxygen-deficient conditions, the electrons were semiconductive and less mobile.[13]

Pekala and co-workers reported the temperature dependence of the Seebeck coefficient of $Ba_{0.74}K_{0.57}BiO_{3.07}$, which showed a superconducting transition at 27 K.[15] They observed negative Seebeck coefficients of a few μV/K at low temperatures, change of sign of the Seebeck coefficient around 200 K, and positive Seebeck coefficients of a few tens of μV/K at high temperatures. Since their observed variation of Seebeck coefficient with temperature showed a quite similar tendency to our results for the Seebeck coefficient of $BaBi_{0.75}Pb_{0.75}O_{3.00}$, it is probable that coexistence of electrons and holes occurs not only in $BaBi_{0.25}Pb_{0.75}O_{3-\delta}$ but also in $Ba_{1-x}K_xBiO_{3-\delta}$. However, we felt their data were insufficient for curve fitting because the purity of the specimen and the variation of oxygen deficiency during the measurement were not clarified and considered in their study.

V. CONCLUSION

The temperature dependence of the Seebeck coefficient of $BaBi_{0.25}Pb_{0.75}O_{3.00}$ was measured. The Seebeck coefficient was negative (a few μV/K) in the temperature range from 10 to 200 K. Above 200 K, values of the Seebeck coefficient increased and reached ~ 20 μV/K around 873 K. The variation with temperature of the Seebeck coefficient was quantitatively explained by using a model in which coexistence of electrons with high mobility and holes with low mobility was assumed. The temperature dependence of electrical conductivity of $BaBi_{0.25}Pb_{0.75}O_{3.00}$ was also explained by assuming coexistence of mobile electrons and immobile holes. The results from this assumption were consistent with the results of electronic-band calculations. The coexistence of electrons and holes in $Ba_{1-x}K_xBiO_{3-\delta}$ and oxygen-deficient $BaBi_{0.75}Pb_{0.75}O_{3-\delta}$ was also suggested.

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