# Mössbauer studies on novel high-$T_c$ (Sn,Sr)-doped La$_{2-2x}$Sr$_{2x}$Cu$_{1-x}$Sn$_x$O$_4$ superconductors

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## Abstract

For La$_{2-2x}$Sr$_{2x}$Cu$_{1-x}$Sn$_x$O$_4$ ($x = 0.075$, $0.090$ and $0.110$) superconductors, the effects of Sn-doping on local microstructure is studied by means of Mössbauer spectroscopy. The results show that Sn ions in the $4+$ valence state dominantly occupy Cu sites rather than La(Sr) site. In the view of the effective oxygen content (or excess oxygen), the dual role of Sn dopant on the carrier concentration is discussed. We attempt to explain the high transition temperature $T_c$ in (Sr,Sn)-doped La$_{2-2x}$Sr$_{2x}$Cu$_{1-x}$Sn$_x$O$_4$ samples under the model of amphoteric effect of Sn-doping on the concentration. © 1999 Elsevier Science B.V. All rights reserved.

## 1. Introduction

After discovery of high-$T_c$ superconductor La–Sr–Cu–O for 12 years, one of the most important progresses in unraveling the mysteries of cuprates is the ability to condense the myriad experimental results into a diagram that depicts the various regions in the temperature–hole concentration plane [1]. There are two main phase boundaries. One is the transition into a long-range antiferromagnetic state at

$T_N$ in the very low doping regime up to a few percent of holes, another is the transition into the superconducting state with a maximum $T_c$ near about 0.15 hole/$CuO_2$. In a small region between these, spin glass behavior is observed. Remarkably, superconductivity is observed in a rather narrow hole concentration range on a scale from 0 to 1. In the La–Sr–Cu–O system, the main methods inducing holes as carriers are the substitution of $Sr^{2+}$ for $La^{3+}$ ions and the insertion of extra oxygen in La–O layers.

During exploration of other new methods inducing carriers and scrutinizing the relationship between carrier and superconductivity, Che and Zhao [2] de-

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signed a novel kind of (Sr,Sn)-doping $La_{2-2x}Sr_{2x}Cu_{1-x}Sn_xO_4$ compounds under a new concept. It is also expected that $Sr^{2+}$ ions substitute for $La^{3+}$ to provide carriers of hole, and $Sn^{4+}$ ions directly replace for $Cu^{2+}$ on the $CuO_2$ plane to induce extra electron in the conducting layer. Under Che's designation, the number of $Sr^{2+}$ and $Sn^{4+}$ ions always keeps a strictly stoichiometric ratio relation of 2:1, when doping content $x$ increases. It is significant that such double-doping of Sr and Sn would result in an offset of electrons and holes. At least, the offset effect would result in a rather low carrier concentration in $La_{2-2x}Sr_{2x}Cu_{1-x}Sn_xO_4$ compounds. In order to extract the double-doping effect, the samples were annealed in the temperature region from 900°C to room temperature under $Ar_2$ ambience to exclude the effect of extra oxygen localized the center of La tetrahedron. It is clear that according to the widely acceptable diagram of temperature–hole concentration, the compounds of $La_{2-2x}Sr_{2x}Cu_{1-x}Sn_xO_4$ would be not superconducting since there were not enough holes. As we know that only if when there were enough carrier concentration, 0.15 hole/$CuO_2$, induced by $Sr^{2+}$ or extra oxygen in $La_2CuO_4$ matrix, the optimum superconductivity would be realized. In addition, several early works about $La_{1.85}Sr_{0.15}Cu_{1-x}Sn_xO_4$ superconductors have confirmed the disrupting effect of Sn-doping on superconductivity [3–6]. Sn directly occupy Cu site on $CuO_2$ plane, which would deteriorate integrality of $CuO_2$ plane. Thus, $Sn^{4+}$ doping itself strongly decrease superconducting transition temperature.

However, Che's recent results have shown that in double-doping $La_{2-2x}Sr_{2x}Cu_{1-x}Sn_xO_4$ compounds, the superconducting critical temperature keeps higher values, even $T_c$ can reach about 33 K for the sample with $x = 0.11$. This (Sr,Sn)-doping effect is completely different with the Sn-doping $La_{1.85}Sr_{0.15}Cu_{1-x}Sn_xO_4$ superconductors in which $T_c$ decreases to 27 K for $x = 0.1$ [3]. It is evident that there might be a new mechanism of Sn-doping on carrier concentration and superconductivity, or it may be said that such (Sn,Sr)-doped $La_{2-2x}Sr_{2x}Cu_{1-x}Sn_xO_4$ compound is perhaps a new system of high-$T_c$ superconductors. This novel phenomenon is doubtful, and stimulates us to investigate the intrinsic relation of carrier and superconductivity on $La_{2-2x}Sr_{2x}Cu_{1-x}Sn_xO_4$ cuprates.

It is rather clear for the effect and site occupation of $Sr^{2+}$ ion in the $La_2CuO_4$ system. However, until now there still has been deficient of the details about Sn dopant such as valence, site occupation and coordination. Especially, Sn ion is a multivalent cation of $Sr^{2+}$ and $Sn^{4+}$. There are some stumbling points about the state of Sn ion in $La_{2-2x}Sr_{2x}Cu_{1-x}Sn_xO_4$, and the explanations for such effect of Sr/Sn doping are full of contradiction. For example, if Sn had been in a state of $Sn^{2+}$ rather than $Sn^{4+}$ which is widely acceptable, Sn ion would have occupied $La^{3+}$ site in a rather high state possibility according to their ionic size. Therefore, $Sn^{2+}$ ions might behave the effect similar to $Sr^{2+}$ ions to provide holes. Therefore, the prerequisite to clarify the qualm about the new mechanism of Sr/Sn-doping is to confirm the details of valence and microstructure of Sn ions in $La_{2-2x}Sr_{2x}Cu_{1-x}Sn_xO_4$ compounds.

Mössbauer spectroscopy is a microscopic method for local structure determination via a series of hyperfine interaction parameters, with provides information on the local site symmetry and ionic valence at a given Mössbauer nucleus. For that reason we have used $^{119}$Sn Mössbauer spectroscopy using the 3/2–1/2 nuclear $\gamma$ resonance at 24 keV in order to obtain information on the valence and the local structure at the Sn site in the $La_{2-2x}Sr_{2x}Cu_{1-x}Sn_xO_4$ compounds. The Mössbauer results of the samples of different doping contents can provide rich and helpful information for study on the relation between carrier concentration and superconductivity. Further, under the basis of the Sr/Sn doping $La_{2-2x}Sr_{2x}Cu_{1-x}Sn_xO_4$ compounds, there might be a chance to find a new high-$T_c$ superconductor.

## 2. Experimental

Single phase polycrystalline $La_{2-2x}Sr_{2x}Cu_{1-x}Sn_xO_4$ ($x = 0$, 0.075, 0.090 and 0.110) superconductors were prepared by solid-state reaction [2]. It is worthwhile to notice that these samples underwent a post-annealing process under $Ar_2$ ambience in order to deoxidize the extra oxygen on the $La_2O_2$ layer. For the samples with different (Sr,Sn) contents, in order to contrast conveniently their physical and structural properties, all the samples were prepared

under the same technological conditions and thermal processes [2].

Superconducting transitions were determined both resistively and magnetically. The ac susceptibility was measured by a mutual-inductance method. The dc resistivities were obtained by the standard four-probe method in a cryostat. For samples annealed at different temperature under $Ar_2$, the critical super-conducting temperature is not changed. Especially, for rather high Sn-doping sample with $x = 0.11$, its $T_c$ also keeps a higher temperature, $T_c \sim 33$ K.

The resulting powders were characterized by X-ray diffraction in the Bragg–Brentano geometry with Cu $K_\alpha$ radiation in Rigaku rotating anode X-ray diffractometer. Powder X-ray diffraction showed the samples to be single phase.

The Mössbauer effect was measured using Ca $^{119}SnO_3$ source which is held at room temperature and driven with triangle mode. The Mössbauer measurements were performed using the 24 keV $\gamma$ transition in $^{119}Sn$ and 50 $\mu$m palladium filter to reduce the concomitant source X-ray. The velocity scale was determined from the quadrupole splitting of $CaSnO_3$ at room temperature.

## 3. Results and discussion

Fig. 1 shows the $^{119}Sn$ Mössbauer spectra with $x = 0.075$, 0.090 and 0.110 at room temperature. All the spectra were paramagnetic and could be repro-duced mostly by imposing one doublet. The Möss-bauer hyperfine interaction parameters were obtained using a least squares fitting program assuming a pure quadrupole interaction, and are summarized in Table 1. The linewidths in three patterns were nearly close to the nature line width of $CaSnO_3$. Attempts to fit more than one Lorentzian resulted in poorer fits. For three samples with different $x$, the isomer shifts $\delta$ of the doublet is rather close to zero velocity (0 mm/s).

Similar to other Sn-doped La-, Y-, and Bi-system cuprates, here the values of the quadrupole splitting $\Delta$ and of the isomer shift $\delta$ are typical for the $Sn^{4+}$ state in Sn compounds. By further scrutiny, our $^{119}Sn$ Mössbauer isomer shifts at room temperature on superconducting $La_{2-2x}Sr_{2x}Cu_{1-x}Sn_xO_4$ ($x = 0.075$, 0.090 and 0.110) are similar to that
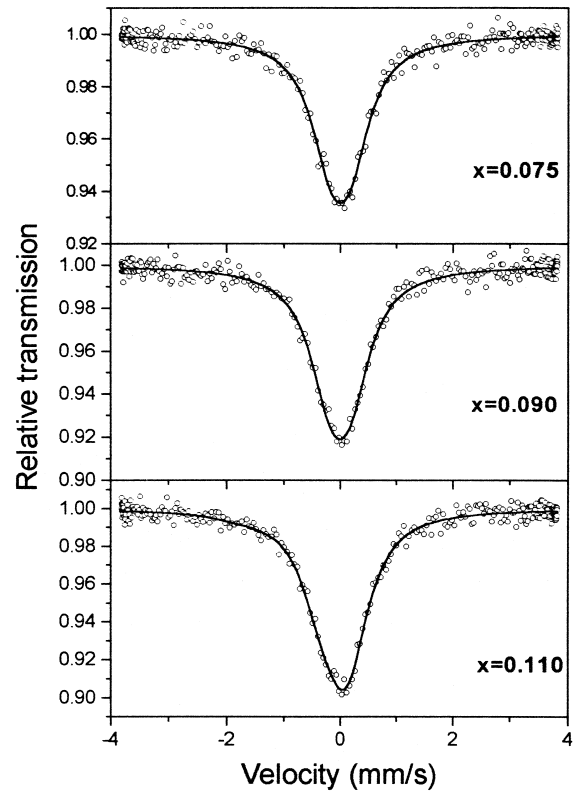


Fig. 1. Mössbauer absorption spectra of $La_{2-2x}Sr_{2x}Cu_{1-x}Sn_xO_4$ ($x = 0.075$, 0.090 and 0.110) at room temperature.

found in superconducting $La_{1.85}Sr_{0.15}Cu_{0.95}Sn_{0.05}O_4$ ($T_c \sim 30.2$ K) [3] and are clearly different with those of $La_{1.85}Sr_{0.15}Cu_{0.95}Sn_{0.05}O_4$ ($T_c < 20$ K) [5], and nonsuperconducting $La_{1.25}Nd_{0.6}Sr_{0.15}Cu_{0.995}$-$Sn_{0.005}O_4$ [7] and $La_2Cu_{0.99}Sn_{0.01}O_4$ [4]. It is evident that the isomer shift is sensitive to the preparation process and stoichiometric compositions. However, to understand these changes, it is crucial to establish the site occupancy and oxygen stoichiometry of doped materials.

For La-214 perovskite with the $K_2NiF_4$ structure, it is widely acceptable that $Sn^{4+}$ ion always occupies B-site rather than A-site [3–7]. In analogy with these compounds, we assigned the $Sn^{4+}$ ion on Cu site in $La_{2-2x}Sr_{2x}Cu_{1-x}Sn_xO_4$. First, based on ionic size considerations, it appears that the Sn impurity substi-tutes on the Cu site since the ionic radius for $Sn^{4+}$ ($r = 0.71$ Å) is very close to that of $Cu^{2+}$ ($r = 0.72$ Å). In addition the ionic radius of $Sr^{2+}$ ($r = 1.33$ Å)

Table 1
Hyperfine parameters of $La_{2-2x}Sr_{2x}Cu_{1-x}Sn_xO_4$ samples at room temperature

| $La_{2-2x}Sr_{2x}$-$Cu_{1-x}Sn_xO_4$ | $\delta$ (mm/s)[a] | $\Delta$ (mm/s) | $\Gamma$ (mm/s) |
|---|---|---|---|
| $x = 0.075$ | $-0.007(1)$ | $0.35(3)$ | $0.87(3)$ |
| $x = 0.090$ | $-0.009(6)$ | $0.36(3)$ | $0.89(4)$ |
| $x = 0.110$ | $-0.015(5)$ | $0.38(3)$ | $0.92(3)$ |

$\delta$: isomer shift, $\Delta$: quadrupole splitting, $\Gamma$: line width at half maximum.
[a]$\delta$: Isomer shift with respect to $CaSnO_3$.

and $La^{3+}$ ($r = 1.15$ Å) are even larger than that of $Sn^{4+}$ ion. It is clear that the occupation of $Sn^{4+}$ ion for La(Sr) site could result in a large energy of lattice distortion which would deteriorate the phase stability. Therefore, under the condition of $4+$ valence, $Sn^{4+}$ ion occupies Cu site. On the other hand, if Sn were in $Sn^{2+}$ rather than $Sn^{4+}$ state, $Sn^{2+}$ ion would occupy A-site in a higher possibility [8] since the radius of $Sn^{2+}$ is 1.02 Å close to those of $La^{3+}$ and $Sr^{2+}$ ion. However, for our preparation process of samples at high temperature and atmosphere, which is not beneficial to the formation of $Sn^{2+}$ state. Moreover, by using $^{119}Sn$ Mössbauer spectroscopy, $Sn^{4+}$ ions (but $Sn^{2+}$ ions) are confirmed to be in all system high-$T_c$ superconductors without exception [3–10].

Secondly, for Sn perovskites such as $CaSnO_3$, $BaSnO_3$, $Ba_2SnO_4$, $Sr_2SnO_4$, and so on, their chemical structures are considerably stable. Sn always occupies B-site and forms an orthorhombic Sn–O six coordination. Based on the similarity of crystallographic structure and stoichiometric composition, it is reasonable that $Sn^{4+}$ ion occupies Cu lattice site in $La_{2-2x}Sr_{2x}Cu_{1-x}Sn_xO_4$ compounds.

Thirdly, in the system of $La_{1.85}Sr_{0.15}Cu_{1-x}Sn_xO_4$, superconducting transition temperatures and volume fractions decrease with the increase of the Sn concentration [3,5]. $T_c$ decreased gradually with $x$ at an average rate $\Delta T_c/\Delta x \sim 0.8$ K/at.% Sn [3] or a larger rate [5]. These results imply that the superconductivity of the Cu oxide is remarkably disturbed by Sn impurities. It seems certain that Sn atoms are being substituted for Cu sites. In our samples, $Sn^{4+}$ ion is also assigned with Cu site although there is not an sharply decrease of $T_c$ similar to $La_{1.85}Sr_{0.15}$-$Cu_{1-x}Sn_xO_4$, since for our (Sr,Sn)-doped $La_{2-2x}$-

$Sr_{2x}Cu_{1-x}Sn_xO_4$ samples, there would be a new mechanism of carrier on superconductivity, which will be discussed below. Therefore, The doublet shown in Fig. 1 is assigned with Cu site on $CuO_2$ plane.

As shown in Fig. 1 and Table 1, linewidths of Mössbauer spectra for samples with different $x$ content are narrow and close to the nature width of source. It shows that the local lattice environments of $Sn^{4+}$ ion trend simplex, namely $Sn^{4+}$ ions dominantly occupy Cu sites and not form the other impure phases containing Sn. This result is also confirmed by Che's X-ray diffraction analysis [2].

In addition, for the sample of $x = 0.075$, 0.090 and 0.110, the quadrupole splitting of the $Sn^{4+}$ ion is only 0.35, 0.36 and 0.38 mm/s, respectively. Such small quadrupole splitting implies that the Sn site possesses a locally high symmetry, i.e., with a Sn–O octahedral coordination. Quadrupole splitting is dominantly determined by the configuration of surrounding Sn ion because of the spherical symmetry of the inner electrons of $Sn^{4+}$ itself. For the $Sn^{4+}$ ion, the quadrupole splitting $\Delta = (1/2)eQV_{zz}(1 + \eta^2/3)^{1/2}$ comes dominantly from the electric field gradient $V_{zz}$ of asymmetric lattice charges surrounding Sn ion. Here $Q$ is the quadrupole moment of the exited state, and asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$, ($0 \leq \eta \leq 1$), is a measure of the deviation of the local symmetry in the vicinity of the Sn nuclei from axial symmetry with a more than two-fold rotational axis. It is obvious that, for the (Sr,Sn)-doped $La_{2-2x}Sr_{2x}Cu_{1-x}Sn_xO_4$ samples, the small quadrupole splitting and narrow absorber line width strongly imply most Sn sites with a high symmetric microstructure. These results rule out the possibility that Sn ions substitute La(Sr) sites. As discussed above, if Sn ion occupied La(Sr) site, there would be a huge lattice distortion surrounding Sn ion due to the large difference ionic size and valence. The high symmetry would be broken by defects, which results in a larger electric field gradient $V_{zz}$ on Sn site. Moreover, the local fluctuations of the electric field gradient caused by the distribution of defects must result in a broadened resonance line. These go against the experimental observation of small quadrupole splitting and narrow line width in (Sr,Sn)-doped $La_{2-2x}Sr_{2x}Cu_{1-x}Sn_xO_4$ samples. Therefore, combining with manifold Mössbauer parameters, it is

evident that Sn dopants are in $Sn^{4+}$ state and dominantly occupy Cu sites with the octahedral oxygen coordination.

Retaining to the discussion about the quadrupole splitting, $Sn^{4+}$ ions enter lattice and occupy Cu sites to lead to local environments that are not always characteristic of the host Cu cations. The Sn–O bond length within $CuO_2$ plane and the bond length of Sn and apical oxygen would respectively product a subtle change relative to previous Cu–O bond lengths due to the shorter ionic radius and higher valence of $Sn^{4+}$ ion. For the quadrupole splitting of 0.35 mm/s in $x = 0.075$ sample, we estimate roughly the bond length of Sn and apical oxygen would shorten about 10% by using the point-charge model.

Sn dopants directed at Cu sites are known to systematically alter crystallographic and superconducting properties. For different (Sr,Sn)-doping samples, the Mössbauer hyperfine interaction parameters smoothly vary with doped concentration increasing, as shown in Fig. 2. The line width appears a increasing trend with (Sr,Sn)-doping. This displays that at the higher doping level, the local lattice distortion induced by Sn dopant is more noticeable. The experimental line with $\Gamma$ increases with (Sr,Sn)-doping content, which results from high Sn-doping leads to an inhomogeneous distribution of the local environment on Sn site. However, the dominant occupancy is still on regular copper sites at this time.

Moreover, Sn as a dopant appears to be present in a higher charge state ($Sn^{4+}$) than the Cu cation

$(Cu^{2+})$, attracting additional oxygen intensively localized surrounding $Sn^{4+}$ ion itself. According to the local structure in vicinity of $Sn^{4+}$, there seem to be not any interstitial sites to accommodate for excess oxygen [11]. However, $Sn^{4+}$ ion still can tenaciously increase the effective oxygen content by other avenues such as, the mentioned above, shortening of Sn–O bond and increase of oxygen occupancy. Since this effective oxygen content (or excess oxygen) is dominantly dependent on the valence and the amount of doping of Sn elements, the excess oxygen is firmly controlled by high valence $Sn^{4+}$ ion and is rather stable in the lattice of $La_{2-2x}Sr_{2x}Cu_{1-x}Sn_xO_4$ samples. Therefore, this kind of excess oxygen close to $Sn^{4+}$ keeps secureness even the sample is annealed under $Ar_2$ in high temperature. However, the excess oxygen discussed here is completely different with one induced by high oxygen pressure or electrochemical oxidization. The latter extra oxygen is believed to be inserted into an interstitial site in the $La_2O_2$ layer block [12,13] and to be in metastable state in high temperature. So this extra oxygen can be easily decontaminated by annealing under $Ar_2$ atmosphere in high temperature.

In view of the effective oxygen content (or excess oxygen) [14], we try to explain the high transition temperature $T_c$ in (Sr,Sn)-doped $La_{2-2x}Sr_{2x}$-$Cu_{1-x}Sn_xO_4$ samples. In our discussion, the effect of the extra oxygen inserting on the $La_2O_2$ layer have been neglected because our samples were annealed under $Ar_2$ at high temperature in order to remove the extra oxygen. In (Sr,Sn)-doped $La_{2-2x}Sr_{2x}Cu_{1-x}Sn_xO_4$ samples, Sn dopant has an importantly amphoteric role on the carrier concentration. On the one hand, the valence of $Sn^{4+}$ ion is obviously higher that of Cu, $+2.21$ [15]. Because the hole acts as the carrier on $CuO_2$ plane, Sn dopants as donors can give more electrons to $CuO_2$ layers to decrease the carrier concentration on $CuO_2$ layers. On the other hand, $Sn^{4+}$ could increase the effective oxygen content in the vicinity of $CuO_2$ plane by increasing oxygen occupancy and shortening of the Sn–O band length, this is equal to bringing excess oxygen into lattice. Sn might act as an acceptor increasing the hole carrier concentration. This dual or amphoteric role of Sn dopant in $CuO_2$ planes is an important effect. It explains why the Sn dopant on Cu site is not detrimental to $T_c$, but may in
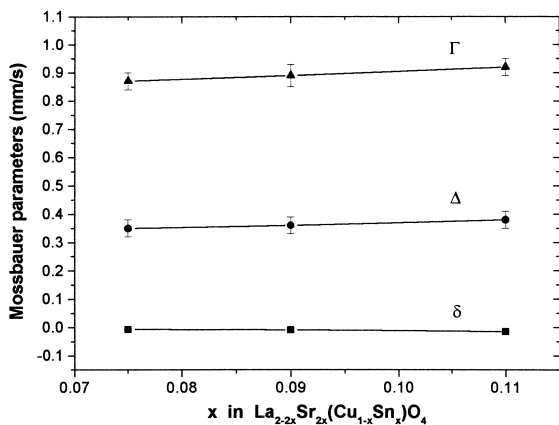


Fig. 2. Mössbauer parameters in $La_{2-2x}Sr_{2x}Cu_{1-x}Sn_xO_4$ compounds with different (Sr,Sn)-doping contents.

fact help increase it by increasing the carrier concentration.

For our $La_{2-2x}Sr_{2x}Cu_{1-x}Sn_xO_4$ samples, in addition to Sr dopant, the competition between two kinds of effects of $Sn^{4+}$ ion results in that the carrier concentration in the $CuO_2$ plane approaches its optimum. So the superconducting transition still occurs at a higher temperature even (Sr,Sn) doping reaches $x = 0.11$. The important difference of carrier concentration between $La_{2-2x}Sr_{2x}Cu_{1-x}Sn_xO_4$ and $La_{1.85}$-$Sr_{0.15}Cu_{1-x}Sn_xO_4$ leads to different superconducting behaviors. It is clear that the crux of maintaining a higher $T_c$ in $La_{2-2x}Sr_{2x}Cu_{1-x}Sn_xO_4$ is to keep a stoichiometric composition of Sr:Sn = 2:1. In this situation, the carrier concentration is close to optimum, while in the $La_{1.85}Sr_{0.15}Cu_{1-x}Sn_xO_4$ system, besides of Sr doping, the amphoteric effect of $Sn^{4+}$ on the carrier concentration could provide more carriers in the $CuO_2$ plane which could correspond to overdoped situation. So $T_c$ always decreases monotonously with Sn doping. It is worth noting that a similar phenomena occur in high (Sn,Pb)-doping $(Bi_{1-x}Sn_{0.5x}Pb_{0.5x})_2Sr_2CaCu_2O_y$ (Bi-2212) system superconductors [16,17]. There is no large detrimental effect on superconducting behavior. At light doping level of (Sn,Pb), the superconducting transition temperature can reach $\sim 90$ K, even in heavy doping level, when $x$ increases to 40%, $T_c$ still can be kept above 70 K [16]. Although at the moment, there is an argument about the site occupancy and the effect of Sn-doping on superconductivity, the salient characteristic of Sn doping should be paid to enough attentions. The final resolution for high-$T_c$ under Sn-doping would presage a discovery of a new Sn-system superconductor.

In conclusion, by means of Mössbauer spectroscopy, the local microstructure induced by Sn-doping is studied in $La_{2-2x}Sr_{2x}Cu_{1-x}Sn_xO_4$. The results show that $Sn^{4+}$ ions occupy Cu sites and increase effective oxygen content. In view of excess oxygen, we discuss the dual role of Sn dopant on the carrier concentration and explain the reason why $La_{2-2x}Sr_{2x}Cu_{1-x}Sn_xO_4$ can keep higher $T_c$ at heavy Sn doping by means of the model of amphoteric effect of Sn-doping on the concentration.

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