Mössbauer study on Sn-doped \((\text{La}_{1-x}\text{Sr}_x)\text{Cu}_{1-x}\text{Sn}_x\text{O}_4\) superconductors under a new concept

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Abstract \(^{119}\)Sn Mössbauer research is carried out on \((\text{La}_{1-x}\text{Sr}_x)\text{Cu}_{1-x}\text{Sn}_x\text{O}_4\) (\(x = 0.075\) and \(0.110\)) superconductors which are designed under a new concept. The Mössbauer spectra results show that Sn occupies Cu position in Sn\(^{4+}\) state, and there is no Sn\(^{2+}\) ion occupying La position. The local lattice deformation near Sn\(^{4+}\) site is small, but displays an increasing tendency with Sn doping. For \(\text{La}_2\text{CuO}_4\) matrix, the simultaneous dopings of Sr/Sn induce holes and electrons on CuO\(_2\) layer in a new mechanism which influences superconductivity. Under a new mechanism of extra oxygen, the extra oxygen effect of Sn-doping on superconductivity is discussed.

Keywords: \((\text{La}_{1-x}\text{Sr}_x)\text{Cu}_{1-x}\text{Sn}_x\text{O}_4\), Mössbauer spectra, local lattice deformation, extra oxygen.

Since the discovery of high \(T_c\) superconductor, one of the most important achievements in copper oxide superconductors is the description of the high \(T_c\) superconductors phase diagram of temperature and hole-density as a whole\(^{[1]}\). Insulated \(\text{La}_2\text{CuO}_4\) matrix possesses long distance antiferromagnetic order. The hole carriers induced by doping result in antiferromagnetic coupling intensity depressed. With the continuous increment of carrier density, the system goes into superconducting state after experiencing the spin-glass state. And at the concentration of 0.15 holes per CuO\(_2\) layer, the superconducting transition temperature reaches its maximum. There are two kinds of ways to induce hole carrier concentration. One way is to substitute partially trivalent rare-earth ions (La) at position A with bivalent alkaline-earth metals such as (Sr, Ba). The other way is to increase oxygen content in insulating matrix \(\text{La}_2\text{CuO}_4\) to obtain \(\text{La}_2\text{CuO}_{4+x}\) through electrochemistry or other methods. The extra oxygen locates at the center of the tetrahedron of La ions\(^{[2]}\). The introduction of extra oxygen can reach the aim of increasing carrier density of CuO\(_2\) layers as well. A lot of experimental results show that inducement of holes under antiferromagnetic background is consanguinely related with superconductivity.

The research on La-214 system with Sn doping started earlier\(^{[3–7]}\). The initial idea was to perform \(^{119}\)Sn Mössbauer measurements in order to investigate the vibrating behavior of lattice, magnetic order and the electronic and structural transitions. The relationship between the introduction of carrier, the transport properties and superconductivity, however, had not been done e-
nough, not to say well.

During studying the influence of the different carrier inducing ways on superconductivity, Che designed a set of cuprate oxide superconductors \((\text{La}_{1-x}\text{Sr}_x)_2\text{Cu}_{1-x}\text{Sn}_x\text{O}_4\) under a completely new concept in which Sr and Sn are doped in a ratio of 2:1. They obtained single phase samples with very good quality. The designation under this new concept is to substitute La with partially Sr\(^{2+}\) dopant to introduce hole carriers, at the same time, to substitute Cu with partially Sn\(^{4+}\) dopant to introduce directly electrons on the CuO\(_2\) layer. According to the nominal composition of \((\text{La}_{1-x}\text{Sr}_x)_2\text{Cu}_{1-x}\text{Sn}_x\text{O}_4\), the holes and electrons induced by doping of Sr and Sn had been keeping with 1:1 ratio nominally. The post-processing of deoxidization had been used during the samples preparation, i.e., annealing the samples under argon atmosphere for a long time to get rid of oxygen from the samples so as to diminish the influence caused by the extra oxide lying at the center of La tetrahedron\(^8\).

According to the phase diagram about temperature and carrier density, and the popular viewpoints of the relationship between superconductivity and carrier density, if keeping high \(T_c\) superconductivity, the CuO\(_2\) layer cannot be substituted. So the Sn doping must cause a sharp decrement of \(T_c\). Furthermore, the electrons induced by Sn doping have the same concentration as the holes because the nominal dopants of Sr and Sn keep 2:1. Thus the carrier density will be depressed greatly or even counteracted. These samples will surely lose the superconductivity in \((\text{La}, \text{Sr})_2\text{CuO}_4\) due to lack of enough carriers. But to our surprise, for \((\text{La}_{1-x}\text{Sr}_x)_2\text{Cu}_{1-x}\text{Sn}_x\text{O}_4\) compounds, the measurement of superconductivity displayed that there is no symptom of \(T_c\) depression during the increment of Sn content \(x\) with the synchronous increment of Sr dopant. And even at \(x = 0.11\), the sample can still maintain good superconductivity of \(T_c \sim 36\) K. This is completely different from the phenomenon in \(\text{La}_{1.85}\text{Sr}_{0.15}\text{Cu}_{1-x}\text{Sn}_x\text{O}_4\), where there is a \(T_c\) decrement of a magnitude of 0.8 K/at.\% Sn observed by others\(^{3,5}\). Obviously, the \((\text{La}_{1-x}\text{Sr}_x)_2\text{Cu}_{1-x}\text{Sn}_x\text{O}_4\) superconductors obtained under new concept design have a totally different mechanism in the effect on carrier density compared with \(\text{La}_{1.85}\text{Sr}_{0.15}\text{Cu}_{1-x}\text{Sn}_x\text{O}_4\) superconductors. To explain this new phenomenon in detail, the Sn ionic valence, the substitution of lattice positions, the local environment and deformation of the lattice should be studied further. Thanks to the \(^{119}\text{Sn}\) Mössbauer spectroscopy is very sensitive to the local environment of Sn, we will report the results of Mössbauer spectra in this paper. Aiming at determining the substitution and ionic valence of Sn ion, thus to provide further information for studying the superconductivity and carrier density in this new system copper superconductors. This will not only benefit for the thorough discussion about the relationship of magnetic order, carrier density and superconductivity, but would also provide a good chance for the discovery of new high-\(T_c\) superconductor.

1 Experiments

The \((\text{La}_{1-x}\text{Sr}_x)_2\text{Cu}_{1-x}\text{Sn}_x\text{O}_4\) single phase samples doped with different Sn (\(x = 0.075, 0.110\)) were made by mixing chemically pure \(\text{La}_2\text{CO}_3\), \(\text{SrCO}_3\), \(\text{CuO}\) and \(\text{SnO}_2\) (\(^{119}\text{Sn}\) content 8.58\%) of appropriate proportion using solid state reaction method. All the samples were made through the same preparation technique in order to be compared and analyzed for different Sn content. The samples were then post-processed under Ar\(_2\) atmosphere from room temperature to 900°C.