Influence of Sintering Temperatures on the Electronic Structures of the Composites $(La_{1.85}Sr_{0.15}CuO_4)_{0.75}(Nd_{1.85}Ce_{0.15}CuO_4)_{0.25}$

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***Abstract*—**The electronic band structure around the Fermi level was crucial for superconductors. However, in composite materials, the systematic investigation of sintering temperatures on the electronic structures was rare. In this study, the effect of sintering temperatures on the electronic structures of the composites of $(La_{1.85}Sr_{0.15}CuO_4)_{0.75}(Nd_{1.85}Ce_{0.15}CuO_{4)0.25}$ was investigated systematically. The X-ray diffraction patterns indicated that: The samples had high quality. At high sintering temperatures, the large interaction between grain boundaries of the two phases happened and it can lead to the variation of lattice parameters. By using synchrotron radiation X-ray, it was found that the electronic band structures just below the Fermi level were difficultly influenced by sintering temperatures. Whereas, the electronic band structures above the Fermi level was easily affected by the sintering temperatures. The experimental results were useful for post thermal treatment of the composite materials.

***Keywords*—**composites, electronic band, lattice structures, superconductivity

I. Introduction

THE copper oxide superconductor is one of the materials being considered as potential candidates for superconducting applications. After a long research processes, some questions of superconductivity have been resolved. However, intriguing questions still exist, such as the pseudogap [1]-[3], stripe phase [4], [5], and electronic phase separation [6]-[8]. Compared with other cuprates, the material of $La_{1-x}Sr_xCuO_4$ (LSCO) has simple structure of perovskite, so the LSCO is the most common materials used to investigate superconducting problems. Recently, many research results are investigated using composite materials. The advantage of studying superconductivity by composite material is that: on the one hand, the superconducting plane CuO_2 avoids being destroyed, so the electronic transport channels are not damaged. On the other hand, the doping material can impose effect, such as anti-ferromagnetism or ferromagnetism, on the superconducting materials and it can produce novel phenomenon. If the amount of doping materials is fixed, by carefully modulate the sintering temperatures, the effect of sintering temperature on structure can be produced by the grain-boundaries of the two kinds of materials. In order to study the effect of anti-ferromagnetic material of $Lu_2Cu_2O_5$ (LCO) on superconducting properties of LSCO, the composite material of $(LSCO)_x(LCO)_{1-x}$ was studied [9]. After doping the LCO, the superconducting transition temperature (T_c) was enhanced. The T_c enhancement was attributed to the tensile strain induced by the differential thermal contraction of the two phases. In the matrix composites of $(La_{1.85}Sr_{0.15}CuO_4)_{1-x}(La_{2/3}Sr_{1/3}MnO_3)_x$, T_c was found to broaden and can be explained as the redistribution of holes in the superconducting system: The magnetic properties of $La_{2/3}Sr_{1/3}MnO_3$ lead to microscopic phase separation in LSCO. Hole-rich and hole-poor regions were formed instead of homogenous [10]. Hsu, et al [11] also identified the electronic phase separation in composite materials. In other superconducting materials, such as $YBa_2Cu_3O_{7-\delta}$ (YBCO), the second phase doping including nanoparticles of metal oxides such as Al_2O_3, Y_2O_3 [12], [13] carbon nanotubes [14], [15] and other compounds [16] has been used to improve the J_c.

However, the effect of sintering temperatures on electronic band structure was rarely studied in composite material, systematically. In composite materials, two kinds of phases exist. After a thermal process, the lattices can interact with each other. Further, the electronic band structures may be affected by the thermal process. In this study, our purpose was to investigate the effect of sintering temperatures on electronic band structures in composite material. The $Nd_{1.85}Ce_{0.15}CuO_4$ (NCCO) was chosen as the doping material, as for that the material had different lattice structures with LSCO. First, after the thermal process, two kinds of lattices can produce strong interaction at the grain-boundaries. Second, the LSCO and NCCO almost had same crystallization temperature, so low sintering temperatures can not destroy any of the two phases after mixing. In order to clarify the effect of sintering temperatures on electronic band structures, the composite material of $(La_{1.85}Sr_{0.15}CuO_4)_{0.75}(Nd_{1.85}Ce_{0.15}CuO_4)_{0.25}$, noted as $(LSCO)_{0.75}(NCCO)_{0.25}$ was synthesized by solid-state reaction method.

II. Experimental Details

The composites of $(LSCO)_{0.75}(NCCO)_{0.25}$ sintered at different temperatures were prepared from LSCO and NCCO polycrystalline powder, respectively. Here, the LSCO and

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NCCO were first synthesized by convenient solid-state reaction method. Appropriate molar quantities of high purity starting oxides La_2O_3, CuO, $SrCO_3$ were mixed. In order to get rid of the element of carbon, the mixed powders were heated at 900 °C for 10 h. The remaining powder was grounded, pressed into pellets, and then sintered at 1250 °C for 30 h. The thermal treatment processes were repeated for three times and with several intermediate grinding in order to obtain high homogeneity. The material of NCCO was also synthesized followed as the above thermal processes. Next, the prepared materials of LSCO and NCCO were mixed according to the ratio of 3:1. Then, the mixed power was divided into five parts, grounded, pressed into pellets, and the pellets were sintered at 250 °C, 600 °C, 800°C, 1000 °C, 1100 °C for 10 h in air atmosphere with intermediate grinding. At last, the remaining powder was ready for experimental measurements.

The X-ray diffraction (XRD) patterns were recorded using Rigaku smart lab powder diffractometer with Cu K_α radiation to check the phase purity and estimate the cell parameters. The X-ray photoemission spectra (XPS) were measured at beamline 4B9B, photoemission spectroscopy station at Beijing Synchrotron Radiation Facility (BSRF). The X-ray absorption near edge structure measurements (XANES) were performed at beamline U7C X-ray absorption station at National Synchrotron Radiation Laboratory (NSRL).

III. RESULTS AND DISCUSSION

The X-ray spectra were measured at room temperature for all the samples. The XRD pattern of experimental samples for LSCO, NCCO, and the composites of $(LSCO)_{0.75}(NCCO)_{0.25}$ (sintered at 250 °C, 600 °C, 800 °C, 1000 °C, 1100 °C) were shown in Fig. 1(a). The XRD spectra of pure samples of LSCO, NCCO were listed for comparison. All the peaks of the two systems can be identified in the composite material without any observable impurity peaks in experimental limit. These results of XRD patterns showed well that the characteristics of composites and the coexisted phases of LSCO and NCCO were compatible with each other. The XRD pattern indicated no observable chemical reaction between the two components during the final sintering. At the lower sintering temperatures (below 800 °C), no peak shift was found. Whereas, as the sintering temperature increasing above 800 °C, the position of the peaks began to move, which indicated that strong interaction happened at the grain-boundaries of the two kinds of materials. So it produced effect on the lattice parameters of the two phases. The lattice parameters of LSCO calculated by the XRD spectra were shown in Fig. 1(b). As the sintering temperatures increased to 800 °C, the samples almost had the same lattices parameters. However, when the sintering temperatures were above 800 °C, the lattice parameters *a* increased and the lattice parameters *c* decreased. At high sintering temperature (above 800 °C), strong interaction occurred induced by grain-boundaries of the two phases. The variations of lattice parameters indicated that the CuO_2 plane of LSCO was stretched and *c* direction was squeezed.

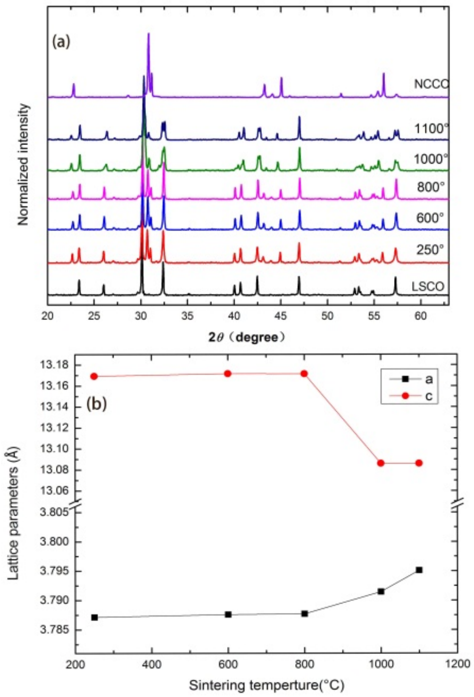

Fig. 1(a): XRD (normalized intensity) patterns for $(LSCO)_{0.75}(NCCO)_{0.25}$ (sintered at 250 °C, 600 °C, 800°C, 1000 °C, 1100 °C) samples measured at room temperature. The pure samples of LSCO, NCCO is for comparison. Fig. 1(b): Variations in the lattice parameters (a and c) of LSCO for all the composite samples at room temperature.

It was commonly believed that the crystal structure was closely related with its electronic band structures [17], [18]. In order to clarify the relation between crystal structure and electronic band structures, the XANES and XPS experiments were performed. It was widely known that the XANES experiments were well suitable to study the electronic band structures above Fermi level. The photons were swept in the energy around and above the absorption edge of the atoms in the compound of interest. Electrons were excited by the absorbed photons. Then the excited electrons can jump into the hybridized orbital and the empty band above Fermi level, so useful information about electronic band around Fermi level can be extracted [18]-[20]. The $5d\delta$ band of Lanthanum in the samples was an unoccupied high-density band and just above the Fermi level [21]. In order to identify the electronic structures around the Fermi level, in the composite materials, the atoms of element lanthanum were chosen as the absorbing atoms.

The Fig. 2 showed the normalized La L_3-edge XANES spectra. It was found that the characteristic white lines occurring near La L_3-edge did not show any shift after the doping. It suggested that the valence of lanthanum did not change after sintered at these temperatures. It was well known that a white line usually gives information for an unoccupied high-density electron state just above a Fermi level and a local partial density-state of an empty conduction band. In the XANES spectra, the peak A as shown in Fig. 2 arises from a $2p$-$5d\delta$ transitions. In Fig.2, the intensity of peak A was gradually decreased as the sintering temperatures increased in all composite samples. The experimental result indicated that the sintering temperatures produced effect on the energy band above the Fermi level: The unoccupied states decreased as the sintering temperatures increased; with the unoccupied states decreasing, the transition probability of the excited electrons decreased which was reflected by the change in the intensity of peak A. So it can be concluded that: in all the sintering temperatures, the unoccupied states just above the Fermi level was gradually decreased as the sintering temperatures increased. The unoccupied states above Fermi level was easily affected by the post thermal processes.

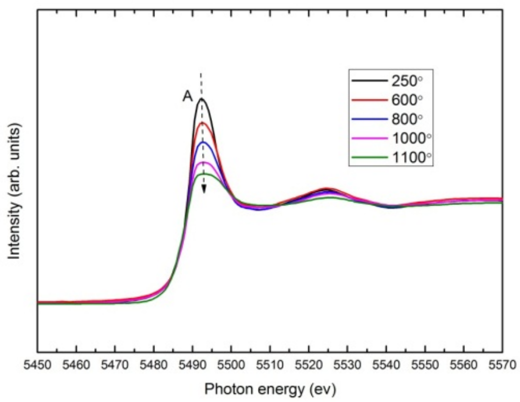

Fig. 2: X-ray absorption spectra near the L_3 edges of La^{3+} ion in the composite samples, taken at room temperature. As the sintering temperatures increasing, the intensity of peak A decreases gradually.

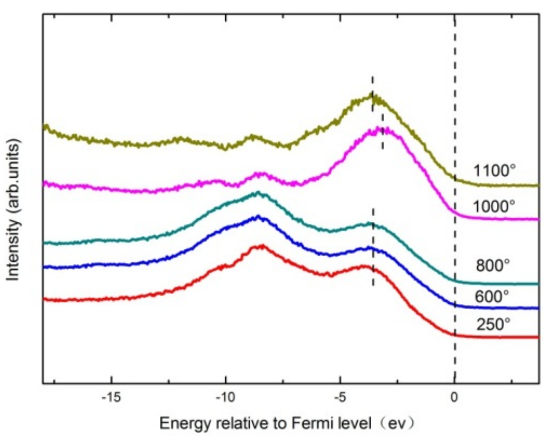

Fig. 3: The valence band of the composite samples. All the spectra are normalized, and the Fermi level is noted by the vertical dotted line.

In order to study the valence band of the composite samples, the XPS experiment was performed. The valence band structure can be probed correctly by the XPS spectra [22]. In this experiment, the valence band spectra were calibrated by C 1s. As shown in Fig. 3, all the composite samples had the same Fermi level. However, the spectra were separated into two groups. As the sintering temperatures increased to 800 °C, the valence band had no change. Whereas, when the sintering temperatures increased to above 800 °C, the structure of the valence band changed. Thus it can be known that: At low sintering temperatures (below 800 °C), the valence band had no change and at high sintering temperatures (above 800 °C), the valence band was affected. The result was also closely related with the XRD spectra. Compared with the unoccupied conduction band, the valence band was more stable. It concluded that the sintering temperatures can produce different effect on the electronic states below and above Fermi level, respectively.

The experiments identifies that the post thermal processes are crucial for the electronic band around Fermi level, so the appropriate post thermal process is necessary in order to study the properties of composite materials.

IV. CONCLUSIONS

The composites of $(LSCO)_{0.75}(NCCO)_{0.25}$ sintered at different temperatures were synthesized by a conventional solid-state reaction method. The crystal structure of the composite material was investigated by XRD experiment. It was found that at low sintering temperatures (below 800 °C), the lattice parameters almost had no change, but at high sintering temperatures, the lattice parameters changed. The CuO_2 plane in the material of LSCO was stretched due to the strain produced by the interaction between grain boundaries and the *c* direction was squeezed. By XPS and XANES experiments, it was found that the sintering temperatures can produce different effect on the electronic band structures around Fermi level: Above the Fermi level, the unoccupied conduction band was easily affected by the sintering temperatures; however, below the Fermi level, the valence band just can be affected at high sintering temperatures (800 °C).

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