



Material characterization of superconducting T' -Nd₂CuO₄ films synthesized by metal organic decomposition

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ABSTRACT

Recently we have achieved superconductivity in T' -RE₂CuO₄ ($RE = Pr, Nd, Sm, Eu, \text{ and } Gd$), films by metal organic decomposition (MOD). In this article, we first report the cation off-stoichiometry effect, which aims at screening out the possibility of hole doping by cation deficiencies. We also investigated the structure and microstructure of superconducting T' -Nd₂CuO₄ films synthesized by MOD. This investigation aims at elucidating why MOD-grown Nd₂CuO₄ films become superconducting whereas our previous Nd₂CuO₄ films grown by molecular beam epitaxy were not superconducting.

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1. Introduction

The parent compounds of high- T_c cuprates have long been believed to be antiferromagnetic Mott insulators. Recently, however, we have reported superconductivity with T_c over 30 K in the parent compounds, T' -RE₂CuO₄ ($RE = Pr, Nd, Sm, Eu, \text{ and } Gd$) [1–3]. The origin of the sharp contradiction between the past and our results can be traced to impurity oxygen (O_{ap}) at the apical site. Superconducting specimens were prepared in thin-film form by metal organic decomposition (MOD). The key recipe to achieve superconductivity in T' -RE₂CuO₄ is low P_{O_2} firing followed by subsequent low-temperature vacuum reduction. We believe that this process cleans up impurity O_{ap} atoms and unveils the property inherent to T' -RE₂CuO₄.

However, a few extrinsic possibilities for superconductivity in T' -RE₂CuO₄ have been suggested, such as electron doping due to oxygen deficiencies and hole doping due to cation deficiencies. In order to exclude the former possibility, one has to determine the site-specific occupancy of oxygen at three sites (regular O(1), O(2) and interstitial O_{ap}) by neutron diffraction experiments within 1–2% accuracy. Such an experiment requires not only high-flux neutron beams but also large specimens with uniform oxygen distribution, which is quite difficult to perform at present. In contrast, one can test the latter possibility rather easily. For example, Yamada et al. demonstrated from the systematic dependencies of the lattice constants and T_c on the cation composition that the oxy-

chloride cuprate with the $K_2NiF_4(T)$ structure, $Ca_{2-x}CuO_2Cl_2$, is a superconductor hole-doped by Ca deficiencies [4,5]. We have performed a similar study of the cation off-stoichiometry effect on T' -Nd₂CuO₄, and obtained a negative result for hole-doped superconductivity due to Nd deficiencies.

Furthermore we have investigated the structure and the microstructure of superconducting films grown by MOD. This aims at clarifying what material features of MOD films are favorable for cleaning up impurity O_{ap} atoms. We have attempted the same low-temperature vacuum reduction to RE₂CuO₄ films grown by molecular beam epitaxy (MBE) but no superconductivity has yet been observed [6]. The difference in the structure and the microstructure between MOD- and MBE-grown films is discussed in this article.

2. Experimental

We prepared Nd_xCuO₄ ($x = 1.4\text{--}2.5$) thin films by MOD using Nd and Cu naphthenate solutions. The naphthenate solutions mixed with Nd: Cu = x : 1 were spin-coated on SrTiO₃ (STO) (0 0 1) substrates. The coated films were first calcined at 400 °C in air to obtain precursors then fired at 850 °C in a tubular furnace under a mixture of O₂ and N₂ while maintaining the oxygen partial pressure at $P_{O_2} = 2 \times 10^{-3}$ atm. Finally the films were reduced in vacuum ($<10^{-4}$ Torr $\approx 10^{-7}$ atm) for $t_{red} = 10$ min at $T_{red} = 420\text{--}440$ °C to remove impurity O_{ap} atoms. The film thickness was typically ~ 800 Å. For a comparison, we also investigated the structure and the microstructure of RE₂CuO₄ films grow by MBE, the details of which are described in [7].

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The structural characterization of the films were performed using two-circle (θ , 2θ) and four-circle (ω , 2θ , φ , ψ) X-ray diffractometers with Cu $K\alpha$ radiations. The out-of-plane orientation was determined by a θ - 2θ scan whereas the in-plane orientation was determined by a φ scan. The structural perfection was assessed by rocking curve measurements. The surface morphology was investigated by an atomic force microscope (AFM). The T_c was determined by resistivity measurements.

3. Results and discussion

3.1. Effect of cation off-stoichiometry

First we describe the effect of cation off-stoichiometry. Fig. 1a shows the θ - 2θ scans of Nd_xCuO_4 films with different starting compositions (x). The Nd-poor film ($x = 1.4$) has XRD peak intensities comparable to the stoichiometric film, whereas the Nd-rich film ($x = 2.5$) has much lower peak intensities. In off-stoichiometric films, impurity phases such as NdO_x or CuO_x were not detected in our two-circle XRD diffractometer. However, large precipitates were observed in Nd-poor films by AFM. Fig. 2 shows the AFM pictures of the Nd_xCuO_4 films with different x . The precipitates observed in the film with $x = 1.4$ were as large as $1 \mu\text{m}$, making the

surface rough (average roughness (R_a) $\sim 150 \text{ \AA}$). In contrast, the Nd-rich film with $x = 2.5$ shows essentially the same morphology as the stoichiometric film. The R_a is 50 – 60 \AA for stoichiometric and Nd-rich films.

Fig. 1b shows the variation of the c -axis (c_0) and a -axis (a_0) lattice parameters for Nd_xCuO_4 films with different x after reduction. The c_0 values were calculated by (00 l) reflections using the Nelson–Riley extrapolation [8] whereas the a_0 values were calculated by (110) and (220) reflections. The bulk values are also shown as dotted lines [9]. Both of the c_0 and a_0 are independent of x in $x = 1.4$ – 2.1 . The c_0 values are $\sim 0.04 \text{ \AA}$ shorter than the bulk value, 12.163 \AA , which is attributed to O_{ap} removal. For the film with $x = 2.5$, c_0 is slightly ($\sim 0.01 \text{ \AA}$) shorter than the values for $x = 1.4$ – 2.1 , and a_0 could not be determined due to poor crystallinity. In the case of superconducting $\text{Ca}_{2-x}\text{CuO}_2\text{Cl}_2$, a_0 shortens with Ca deficiency (x), implying hole doping [5]. In general, hole doping in the CuO_2 planes shrinks the Cu–O bond length due to depletion of electrons in the antibonding $\sigma^*(x^2 - y^2)$ orbitals. In our Nd_xCuO_4 films, however, a_0 and c_0 show almost no sensitivity to the starting composition, indicating that cation vacancies are not created in the T lattice, but instead, excess cation atoms are precipitated out from the T lattice as NdO_x or CuO_x . Hence we dismiss the idea that hole-doped superconductivity occurs via cation deficiencies.

Fig. 3 shows the temperature dependences of resistivity of Nd_xCuO_4 films with different x . The films with $x = 1.4$ – 2.1 show a full superconducting transition, whereas the film with $x = 2.5$ does not show zero resistance. The film with $x = 2.5$ can be judged to be over-reduced from the shorter c_0 value and shape of the ρ - T curve [10]. The smaller grain size of this film, as judged from AFM surface morphology and weaker XRD peak intensities, may be a reason for excessive reduction in spite of the same reduction recipe as for the other films. Fig. 4 summarizes T_c and $\rho(300 \text{ K})$. The T_c is the highest and $\rho(300 \text{ K})$ is the lowest at $x = 2.0$. The cation off-stoichiometry leads to a slight and gradual degradation in T_c and $\rho(300 \text{ K})$ for $x < 2.0$ and to a rapid degradation for $x > 2.0$. The fact that stoichiometric Nd_2CuO_4 shows the best superconducting properties again indicates that the superconductivity in T - RE_2CuO_4 is unlikely to be due to hole doping via cation deficiencies.

3.2. Structural and microstructural characterization of stoichiometric films

Next we show the structure and microstructure of stoichiometric films. Fig. 5 summarizes the results of structural characterization for the films that underwent reduction. The θ - 2θ scan shows that the film is single phase T and c -axis oriented, and that the rocking curve through (006) gives $\Delta\omega$ (full width at half maximum, FWHM) of 0.12° . This value is comparable with $\Delta\omega = 0.11^\circ$ reported for best PLD-grown $(\text{Pr}, \text{Ce})_2\text{CuO}_4$ films on LaAlO_3 substrates [11] and $\Delta\omega = 0.092^\circ$ of our MBE-grown T - La_2CuO_4 films on NdScO_3 substrates [12]. The φ scan shows that the film is also in-plane aligned ($[100]// [100]$) of STO) with $\Delta\varphi$ as small as

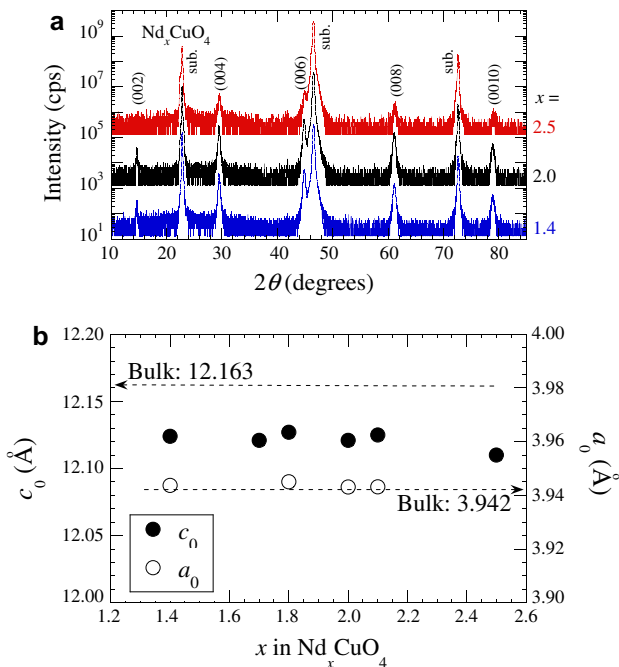


Fig. 1. (a) θ - 2θ scans of reduced films from starting composition Nd_xCuO_4 with different x . (b) Variation of c -axis (c_0) and a -axis (a_0) lattice parameters for reduced Nd_xCuO_4 films with different x . The bulk values are also shown as dotted lines.

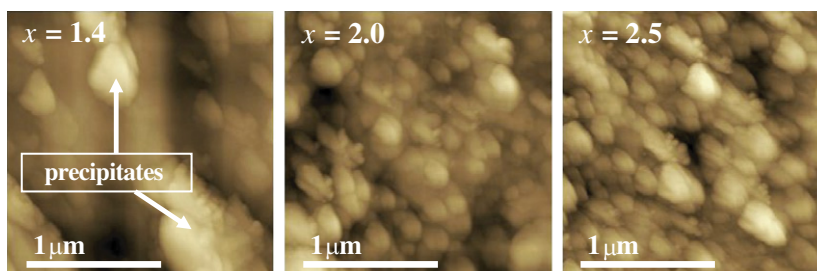


Fig. 2. AFM pictures of the Nd_xCuO_4 films with different x .

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