Journal of Alloys and Compounds, 207/208 (1994) 307–310
JALCOM 3056

The influence of lithium intercalation and iodine on the electrical properties of the superconductor $Nd_{1.82}Ce_{0.18}CuO_z$

Wei Zhao, Li-Quan Chen, Yu-Zhen Huang[a], Lu-Qian Qian[a], Jun-Jie Yue, Lian-Zhong Wang and Zhong-Xian Zhao[a]
Institute of Physics, Chinese Academy of Sciences, [a]National Laboratory for Superconductivity, P.O. Box 603, Beijing 100080 (China)

Abstract

As-prepared $Nd_{1.82}Ce_{0.18}CuO_z$ pellets treated by electrochemical lithium intercalation and iodine vapour were studied. It was found that the sample $Li_{0.06}Nd_{1.82}Ce_{0.18}CuO_z$ intercalated by lithium at 705 °C, using LiF/KF melt electrolyte, became superconductive at $T_c = 23.5$ K. The mechanism is considered to be that lithium has been inserted into the interstitial site near the Cu–O square and has donated its electron to the CuO_2 plane, while the extra oxygen atom has been removed. The insertion of lithium using $LiClO_4$ polypropylene carbonate electrolyte cells at room temperature was very slow and no superconductivity was observed. For these samples with lithium inserted at room temperature and then annealed at 900 °C in air, the defect oxygen atoms can be introduced into the structure along with lithium as shown by the increase of resistivity with the lithium amount. The samples treated with iodine at 200 °C showed a resistivity drop between 9.9 and 13.9 K, which might indicate superconductivity in a small portion with possible composition $Nd_{1.82}Ce_{0.18}CuO_{z-y}I_y$. Combined with the results of the luminescence spectra, the mechanism of deoxygenation can be considered as the delocalization of the doped electrons in the crystal.

1. Introduction

As a class of electron-doped superconductors, $Nd_{2-x}Ce_xCuO_z$ has attracted much attention due to its electrical properties. In this system, as-prepared samples are not superconductive upon Ce doping. Superconductivity occurs over a narrow Ce concentration range ($0.14 < x < 0.18$),only after heat treatment under reducing conditions beyond 700 °C [1,2].The role of reduction treatment is usually considered to remove extra oxygen within the structure and to increase the number of electron carriers through the reduction of Cu^{2+} to Cu^{1+} [3–7]. In addition to Ce- or Th-doped Nd_2CuO_4, the substitution of fluorine for oxygen [6,8] and the intercalation of hydrogen [9] in $Nd_{2-x}Ce_xCuO_z$) have been investigated with the purpose of controlling the carrier concentration through doping. In p-type superconductors, lithium insertion studies have been performed on $YBa_2Cu_3O_7$ [10–12] and a lower T_c of lithiated samples with a small amount of inserted lithium (less than 0.5 per unit cell) was observed [13]. Note that apart from lithium insertion, there have been some similar studies of hydrogen insertion into $YBa_2Cu_3O_7$ [10,14], $Bi_2Sr_2Cu_2O_x$ and $La_{2-x}Sr_xCuO_4$ [15,16] as well as iodine intercalation of $Bi_2Sr_2Cu_2O_8$ [17] and $Bi_2Ca_{2.5}Nd_{0.5}Cu_2O_y$ [18]. In these doped p-type systems, a depression in T_c is always observed, which arises from the decrease in hole concentration by doping. Therefore, it is interesting to study the doping effect of these atoms on the electrical properties of n-type $Nd_{2-x}Ce_xCuO_z$. In this paper, electrochemical lithium intercalation into as-prepared $Nd_{1.82}Ce_{0.18}CuO_z$ has been performed, using a LiF/KF melt electrolyte cell operated at 705 °C and $LiClO_4$ polypropylene carbonate (PC) electrolyte cells at room temperature. The reaction of iodine vapour with as-prepared $Nd_{1.82}Ce_{0.18}CuO_z$ was carried out at 200 °C. The resistivity-temperature dependence as well as luminescence spectra of these treated samples have been studied.

2. Experimental procedures

$Nd_{1.82}Ce_{0.18}CuO_z$ samples were synthesized using high-purity Nd_2O_3, CeO_2 and CuO as starting materials. Mixtures of nominal composition were sintered in air at 950 °C for 12 h and at 1100 °C for 24 h, with intermediate regrinding, pressing into pellets, and cooling together with the furnace. By elemental analysis, the final composition of the samples was determined as $Nd_{1.82}Ce_{0.18}CuO_z$. Some of the samples were reduced in an argon atmosphere at 900 °C for 12 h, which showed bulk superconductivity with $T_c = 23.5$ K.

SSDI 0925-8388(93)03056-O

The redox cells were used at 705 °C as well as at room temperature where the as-prepared samples served as cathodes. The cells at 705 °C were constructed with a $Nd_{1.82}Ce_{0.18}CuO_z$ pellet, LiF/KF melt and Pt anode. The current density was 21 mA/cm^2. The intercalation was carried out over a period of several minutes and then the treated sample was cooled to room temperature with packing a protective electrolyte layer. The cells for lithium intercalation at room temperature were composed of a $Nd_{1.82}Ce_{0.18}CuO_z$ pellet, $LiClO_4$ (1 M)/PC electrolyte and lithium anode. A galvanostat device was used to control the amount of lithium insertion. The current density was 10 μA/cm^2 and the discharge time could be several days depending on the amount of lithium intercalation. After intercalation, these samples were cleaned for resistivity and ac-susceptibility measurements. Solid iodine was sealed in air with as-prepared sample pellets in a stainless steel vessel. The reaction was performed at 200 °C for 2 days. The partial pressure of the iodine vapour was about 1.2 atm.

3. Results and discussion

In Fig. 1, the temperature dependence of the samples before the reduction (Fig. 1(a)) was semiconductor-like. After argon reduction (Fig. 1(b)) and lithium intercalation at 705 °C (Fig. 1(c)) the samples showed a superconducting transition at $T_c^{on} = 23.5$ K which is in good agreement with that determined by ac-susceptibility measurements. It can be seen that besides the same superconducting transition temperature, the temperature dependence of the resistivity of the lithium-inserted sample is different from that of the argon-reduced sample. The former is of smaller resistivity ratio ($\rho(300\text{ K})/\rho(23\text{ K}) = 1.02$) than the latter with a ratio of 1.14. This temperature dependence of the resistivity of the lithium-inserted sample can be explained in terms of composition inhomogeneities [2], because the lithium insertion process occurs inhomogeneously [13]. By elemental analysis, the lithium content of the lithium intercalated sample was determined as $\delta = 0.062$, a value consistent with $\delta = 0.059$, the amount of intercalation determined coulometrically. This consistence indicates that through electrochemical intercalation, lithium atoms have inserted into $Nd_{1.82}Ce_{0.18}CuO_z$ forming $Li_{0.06}Nd_{1.82}Ce_{0.18}CuO_z$. It is worthwhile to note that lithium intercalation into $Nd_{2-x}Ce_xCuO_z$ is not surprising in view of the structural similarity between $Nd_{2-x}Ce_xCuO_z$ and $YBa_2Cu_3O_7$. Both show features such as a layered lattice containing interstitial sites and diffusion path, and mixed oxidation states for copper. These features are required for an intercalation reaction to occur [19]. In $YBa_2Cu_3O_7$, the lithium is considered to occupy the interstitial site near the Cu–O square plane with the most stable structure and it is completely ionized with the donated electron localized on the copper chain [19]. As a result, the hole carrier density in $YBa_2Cu_3O_7$ decreases resulting in a reduction of T_c [13]. By contrast, the superconductivity in $Li_{0.06}Nd_{1.82}Ce_{0.18}CuO_z$ implies that the electron carrier density increases on the CuO_2 plane, *i.e.* the lithium atoms may have been inserted into the site near the Cu–O square plane and donated electrons to the Cu atoms. In our preliminary work, we have not measured the change of oxygen content after lithium intercalation, but because the removal of extra oxygen atoms is critical in the occurrence of superconductivity, we can infer that with lithium intercalation, the process of deoxygenation must also occur. The extra oxygen atoms in the structure have been removed selectively during electrochemical intercalation at 705 °C as indicated by the temperature dependence of the resistivity which reveals that the sample is more inhomogeneous in composition than the argon-reduced sample. Similar work was performed for as-prepared samples doped by hydrogen at 110 °C but no superconductivity was found [9]. The reason remains unclear. An explanation is that the doping of hydrogen atoms does not delocalize the electrons in the crystal due to the relatively low treatment temperature [9]. Subsequently, we will discuss the mechanism of deoxygenation further with reference to the luminescence results.

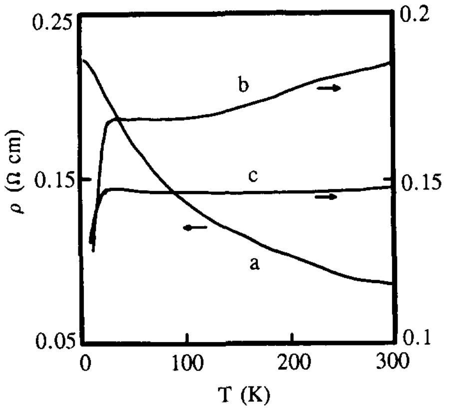

Fig. 1. Resistivity as a function of temperature for as-prepared (a) and Ar-reduced samples (b), and $Li_{0.06}Nd_{1.82}Ce_{0.18}CuO_z$ (c). In the lithiated sample, there is an onset of superconductivity at $T_c \doteq 23.5$ K equal to that of the Ar-reduced sample.

At room temperature, the insertion of lithium into $Nd_{1.82}Ce_{0.18}CuO_z$ is very slow and usually proceeds over several days. This slower diffusion process at room temperature than at 705 °C suggests that the intercalation of lithium in $Nd_{1.82}Ce_{0.18}CuO_z$ is controlled by a dynamic process. The surface resistance of as-treated samples is semiconducting-like and increases with the amount of lithium insertion or insertion time. This may be because the electrolyte PC/$LiClO_4$ with relatively low conductivity deposits onto the surface of the pellets. After cleaning and annealing in air at 900 °C for 6 h with slow cooling to room temperature, the resistivity of these samples is metallic again but no superconductivity is detected. By elemental analysis the final lithium content is ten times less than the amount determined coulometrically due to the escape of lithium during the high temperature anneal. Figure 2 shows the temperature dependence of the resistivity for these samples. It can be seen that the resistivity increases with the lithium amount at each fixed temperature, similarly to the oxygen-partial-pressure dependence of resistivity which showed that the resistivity increases with the increase in the oxygen partial pressure or the decrease in oxygen deficiency [20]. These results indicate that in the samples inserted with lithium at room temperature and then annealed in air at 900 °C, more oxygen atoms were introduced into the structure by lithium during annealing in air. Since the superconductivity of $Nd_{2-x}Ce_xCuO_z$ is closely related to the oxygen deficiency (approximately 0.008 per unit cell in $Nd_{1.85}Ce_{0.15}CuO_z$ as determined in ref. 21 and up to 0.05 per unit cell), these extra oxygen atoms suppress n-type doping in the CuO_2 and therefore the resistivity increases [7].

The temperature dependence of the resistivity for iodine-treated samples is shown in Fig. 3. Samples N1 and N2 were prepared separately. They show semiconductive-like behavior and present a resistivity drop at 13.9 K for sample N1 and at 11.5 K for sample N2. These results are repeatable, showing the resistivity drop ranging over 9.9–13.9 K depending on different samples. We found that after several repeated measurements of the resistivity, the samples showed semiconducting behavior again and such a resistivity drop was no longer observed. This implies that the resistivity drop is caused by a metastable phase which is unstable and can be decomposed with the cycles of measurements. Because the removal of extra oxygen happens only above 400 °C in a N_2 atmosphere [2], it seems impossible that this resistivity drop is caused by the deoxygenation without iodine reaction, *i.e.* this metastable phase should be the product of $Nd_{1.82}Ce_{0.18}CuO_z$ reacting with iodine. As we know that in $Nd_{2-x}Ce_xCuO_z$, the oxygen atoms can be substituted by fluorine atoms [6,8], similarly in $Nd_{1.82}Ce_{0.18}CuO_z$, the iodine atoms may play the same role by forming $Nd_{1.82}Ce_{0.18}CuO_{z-y}I_y$. Microprobe measurements found no evidence for such a second phase, indicating less than ~0.5%. Here we cannot determine whether this compound is a superconductor. One possible explanation is that this compound is superconducting but in a small portion in the pellets with composition inhomogeneities as observed refs. 1 and 2. To confirm this, further measurements using a more sensitive SQUID magnetometer are needed.

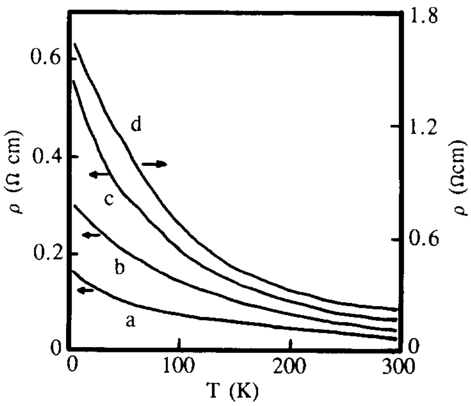

Fig. 2. Resistivity as a function of temperature for $Li_\delta Nd_{1.82}Ce_{0.18}CuO_z$ samples inserted by lithium at room temperature and then annealed at 900 °C for 6 h. (a) $\delta=0.0015$, (b) $\delta=0.0024$, (c) $\delta=0.0032$, (d) $\delta=0.0054$.

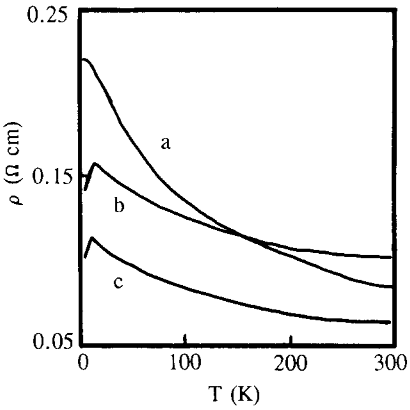

Fig. 3. Temperature dependence of the resistivity for as-prepared sample (a), sample N1 (b) and sample N2 (c) treated with iodine at 200 °C. In samples N1 and N2, corresponding $T_c^{on}=13.9$ K and 11.5 K, respectively.

As discussed above, the role of reduction treatment is currently considered to remove extra oxygen (apical oxygen, fluorite-type oxygen [2], or oxygen in the CuO_2 plane [6]) within the structure and to increase the number of electron carriers in the CuO_2 plane. The dopant electrons are donated to Cu^{2+} leading to Cu^{1+} formation [3–7]. Here we measured the luminescence spectra in order to study the change of copper valence for these treated samples. It was found that the emission band of Cu^{2+} is centered near 900 nm in $YBa_2Cu_3O_7$ [22,23]. From Fig. 4, it can be seen that for as-prepared samples, an emission band peaking at 940 nm is observed, which can be attributed to be mainly from the emission of Cu^{2+} ions [22,23]. A very weak emission intensity is observed from the lithium-inserted sample $Li_{0.06}Nd_{1.82}Ce_{0.18}CuO_z$ with $T_c=23.5$ K. The same result is found in the argon-reduced sample with slightly weaker luminescence. These results are difficult to

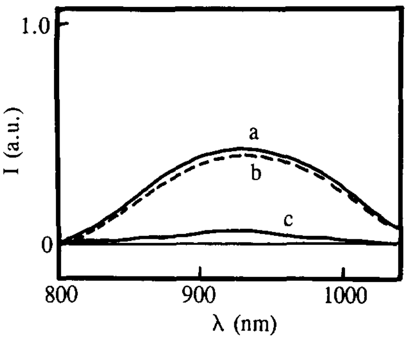

Fig. 4. Luminescence spectra of as-prepared sample (a), iodine-treated sample (b) and $Li_{0.06}Nd_{1.82}Ce_{0.18}CuO_z$ (c) under excitation of an Ar^+ laser beam 476.5 nm.

explain using the above mechanism, because either before or after reduction, Cu^{2+} ions still exist in the samples. It seems that another mechanism is more suitable, *i.e.* the delocalization mechanism [24,25]. According to this mechanism, the luminescence of as-prepared samples can be explained to be from the Cu ions at which the electrons provided by Ce doping are localized with the aid of local disordered potential produced by extra oxygen. The deoxygenation process removes these interstitial oxygens and the associated disordered potential, and the electrons become charge carriers and delocalize in the crystal. Thus the luminescence decreases. In other words, the emission band for the as-prepared sample comes mainly from the Cu^{2+} ions which are coordinated with extra oxygen atoms and can be considered as impurity centers in $Nd_{1.82}Ce_{0.18}CuO_z$. The removal of extra oxygen atoms leads to the decrease in the amount of these Cu^{2+} ions and therefore the intensity of this emission band becomes weak. For the iodine-reacted sample, the emission intensity of this band decreases slightly, suggesting a smaller decrease of these Cu^{2+} ions in this sample, in accordance with the result that the metastable phase $Nd_{1.82}Ce_{0.18}CuO_{z-y}I_y$ is in a small portion.

4. Conclusions

By electrochemical intercalation at 705 °C, the lithiated sample $Li_{0.06}Nd_{1.82}Ce_{0.18}CuO_z$ showed similar superconductivity at 23.5 K to that of the argon-reduced sample. The mechanism is considered to be that lithium atoms were inserted into the interstitial site near the Cu–O square and donated their electrons to the CuO_2 plane; meanwhile the extra oxygen atom was removed. For the samples inserted with lithium at room temperature and then annealed at 900 °C in air, the defect oxygen atoms can be introduced into the structure by lithium as shown by the increase in resistivity with the amount of lithium. The iodine-reacted samples showed a resistivity drop between 9.9 and 13.9 K, which might indicate superconductivity in a small portion with possible composition $Nd_{1.82}Ce_{0.18}CuO_{z-y}I_y$. Combined with the results of the luminescence spectra, the mechanism of deoxygenation can be considered as the delocalization of the doped electrons in the crystal.

References

1 Y. Tokura, H. Takagi and S. Uchida, *Nature, 337* (1989) 345.
2 E. Wang, J.-M. Tarascon, L.H. Greene and G.W. Hull, *Phys. Rev. B, 41* (1990) 6582.
3 S. Uji, M. Shimoda and H. Aoki, *Jpn. J. Appl. Phys., 28* (1989) L804.
4 T. Suzuki, M. Nagoshi, Y. Fukuda, K. Ch-ishi, Y. Syono and M. Tachiki, *Phys. Rev. B, 42* (1990) 4263.
5 M. Klauda, J.P. Strobel, J. Scholtterer, A. Grassmann, J. Markl and G. Saemann-Ischenko, *Physica C, 173* (1991) 109.
6 S.M. Butorin, V.R. Galakhov, E.Z. Kurmaev, S.M. Cheshnitsky, S.A. Lebedev and E.F. Kukovitzkii, *Phys. Rev. B, 47* (1993) 9035.
7 H. Oyanagi, Y. Yokoyama and H. Yamaguchi, *Phys. Rev. B, 42* (1990) 10136.
8 A.C.W.P. James, S.M. Zahurak and D.W. Murphy, *Nature, 338* (1989) 240.
9 K. Kobayashi, Y. Goto, S. Matsushima and G. Okada, *Jpn. J. Appl. Phys., 30* (1991) L1106.
10 H. Eichenbusch, W. Paulus, E. Gocke, J.F. March, H. Koch and R. Schoellhorn, *Angew. Chem., Int. Ed. Engl., 26* (1987) 1188.
11 J. Vondrak, I. Jakubec, J. Bludska and V. Skacel, *Electrochim. Acta, 35* (1990) 995.
12 A. Varez, E. Moran, M.A. Alario-Franco, J. Santamaria, G. Gonzalez-Diaz and F. Sanchez-Quesada, *Solid State Commun., 76* (1990) 917.
13 M.A. Alario-Franco, E. Moran, A. Varez, J. Santamaria and F. Sanchez-Quesada, *Solid State Ionics, 44* (1990) 73.
14 M. Nicolas, J.N. Daou, I. Vedel, P. Vajda, J.P. Burger, J. Lesueur and L. Dumoulin, *Solid State Commun., 66* (1988) 1157.
15 T. Takabatake, W. Ye, S. Orino, T. Tamegai and H. Fujii, *Physica C, 162–164* (1989) 65.
16 T. Ekino, K. Matsukuma, T. Takabatake and H. Fujii, *Physica B, 165&166* (1990) 1529.
17 X.D. Xiang, S. McKernan, W.A. Vareka, A. Zettl, J.L. Corkill, T.W. Barbee and M.L. Cohen, *Nature, 348* (1990) 145.
18 W.J. Zhu, Y.Z. Huang, S.L. Jia, L.Q. Chen, J.K. Liang and Z.X. Zhao, *Proc. Beijing Int. Conf. on High T_c Superconductivity*, Beijing, China, 1992, p. 180.
19 M.S. Islam and C. Ananthamohan, *J. Solid State Chem., 100* (1992) 371.
20 F. Munakata, T. Kawano, A. Nozaki and H. Yamauchi, *J. Mater. Res., 6* (1991) 42.
21 K. Suzuki, K. Kishio, T. Hasegawa and K. Kitazawa, *Physica C, 166* (1990) 357.
22 J.Y. Cai, C.X. Wang, N.G. Wang, S.H. Liu, J.G. Wu, Z.F. Song and S.D. Xia, *Sci. China A, 34* (1991) 1119.
23 Z.F. Song, L.Z. Zhang, W.T. Liu, J.G. Wu and G.X. Xu, *J. Chin. Rare Earth Soc., 7* (1989) 1.
24 S. Kohiki, J. Kawai, T. Kamada, S. Hayashi, H. Adachi, K. Setsune and K. Wasa, *Physica C, 166* (1990) 437.
25 W. Jiang, J.L. Peng, Z.Y. Li and R.L. Greene, *Phys. Rev. B, 47* (1993) 8151.