

Compatibility of Nd and Ba in $\text{YBa}_2\text{Cu}_3\text{O}_y$ Superconductor

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Abstract — A series of samples with nominal compositions of $\text{YBa}_{2-x}\text{Nd}_x\text{Cu}_3\text{O}_y$ were prepared by solid state reactions and investigated by X-ray diffraction, magnetic and electrical measurements. The solubility, x , was determined to be $x < 0.25$. It is found that the solubility of rare earth Re ions at the Ba-sites in $\text{Re}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$ is strongly related to a geometric parameter, the tolerance factor t . For $x < 0.25$, T_{c0} are all above 92K. For $x > 0.3$ T_{c0} drops sharply to about 84K, and finally for $x=0.5$ T_{c0} falls to 30K and T_{c0} is below 10K. Our results suggest that the small compatibility of Nd and Ba in $\text{YBa}_2\text{Cu}_3\text{O}_y$ system does not seriously suppress the superconductivity.

I. INTRODUCTION

It is well known that $\text{ReBa}_2\text{Cu}_3\text{O}_y$ (ReBCO) superconductors show almost the same superconducting transition temperature ($T_c \sim 90\text{K}$) [1]. $\text{YBa}_2\text{Cu}_3\text{O}_y$ (YBCO) is a well-studied electrode material for high- T_c superconductor-normal metal-superconductor (SNS) junctions. Barrier materials with suitable physical properties and good interface character are key factors for the fabrication of reliable and high quality SNS junctions. Various barriers such as $\text{PrBa}_2\text{Cu}_3\text{O}_y$ (PBCO) [2], $\text{Pr}_{1-x}\text{Y}_x\text{Ba}_2\text{Cu}_3\text{O}_y$ [3] and doped YBCO [4] have been used for high- T_c SNS junctions. $\text{NdBa}_2\text{Cu}_3\text{O}_y$ (NBCO) possesses the highest T_c in the Re123 family [5], however, its T_c depends strongly on the fabricating conditions [6]. Since the lattice constants a and b of NBCO match very well with those of YBCO, it could be another good barrier material for SNS junctions. Oh et al [7] have reported on a SNS ramp junction with a NBCO barrier. The interface between the YBCO and NBCO is fairly clean, and the interface resistance is very small. To understand the interface between the YBCO and NBCO layers, it is important to investigate the compatibility of YBCO and NBCO. However, it has been suggested recently that the magnetic rare earth ions at the Ba-sites are fatal to the superconductivity [8]. It is even predicted that PBCO without Pr-at-Ba-site defects should be a superconductor with a $T_c \sim 90\text{K}$. Y^{3+} ion is nonmagnetic, its solubility at the Ba-sites is very limited. Nd^{3+} ion, however, is magnetic ($3.54\mu_B$) and its solubility at the Ba-sites is very wide. Thus the $\text{YBa}_{2-x}\text{Nd}_x\text{Cu}_3\text{O}_y$ system is suitable for as investigation into the effects of magnetic Re ions at the Ba-sites on superconductivity. In this work, we aim to check the compatibility of Nd and Ba and its influence on crystal structure and superconductivity in $\text{YBa}_2\text{Cu}_3\text{O}_y$.

II. EXPERIMENTAL

The samples of $\text{YBa}_{2-x}\text{Nd}_x\text{Cu}_3\text{O}_y$ with $x=0.0, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.50$ were prepared by solid state reactions. The mixture of the powders of Y_2O_3 (99.9%), Nd_2O_3 (99.9%), BaCO_3 (99.5%) and CuO (99.9%) was ground and calcined in air at 970°C for 12h. The resultant powder was reground and sintered in air at 960°C for 12h. After this sintering process the powder samples were examined by x-ray diffraction with CuK_α radiation. After being reground and pelletized, the pellet was fired in air at 960°C for 12h and at 500°C in flowing oxygen (1l/min) for 10h. Finally, the samples were cooled down to room temperature at a slow cooling rate ($1^\circ\text{C}/\text{min}$). The final samples were examined by the x-ray diffraction again.

The resistance vs temperature curves were measured by a standard DC four-probe method. The samples were cooled by liquid nitrogen or a closed-cycled cryogenic system. The cooling rate was controlled to be $2\text{K}/\text{min}$ by a computer program. The temperature was measured by a Pt resistance thermometer. The temperature error was estimated to be less than 0.5K . The susceptibility was measured by an ac mutual inductance method, with an operating frequency of 120Hz .

III. RESULTS AND DISCUSSION

All samples were examined by x-ray powder diffraction. The results indicate that samples with $x < 0.3$ are nearly single Re123 phase. The impurity phase content was estimated to be less than 1wt.%. Fig. 1 shows the x-ray powder diffraction patterns for the samples of $x=0.05, 0.15$ and 0.25 . All the intensities of the (001) diffraction peaks were enhanced strongly, indicating an obvious (001) preferred direction for the bulk samples. The x-ray powder diffraction patterns can be indexed by a tetragonal Re123 lattice. The orthorhombic splitting of (200), (020) and (006) diffraction peaks at $2\theta \sim 46.5^\circ$ is very small (see Fig.2). The solubility of Nd at the Ba-sites in $\text{YBa}_{2-x}\text{Nd}_x\text{Cu}_3\text{O}_y$ is less than 0.25, which is smaller than that in $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$ ($x \leq 0.6$) [9]. The size effect of the rare earth ions is responsible for the reduction in the solubility of Nd.

It is well known that the stability of the perovskite structure can be scaled by a geometrical parameter, i.e. tolerance factor, t . For a ABO_3 perovskite structure the tolerance factor, t , is defined as [10]:

$$t = (r_A + r_O) / \sqrt{2} (r_B + r_O) \quad (1)$$

where r_A , r_B and r_O are the radii of the A, B and O ions, respectively. For $0.8 < t < 1.0$, the perovskite structure can

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be formed. Since the Re123 structure is a distorted layered perovskite structure. The tolerance factor could still be a valid description for the stability of the Re123 structure.

The ion radii of Re^{3+} , Ba^{2+} , Cu^{2+} and O^{2-} [11] were used to calculate the tolerance factors. Table I lists the calculated tolerance factor t values of $\text{ReBa}_2\text{Cu}_3\text{O}_y$. With the increase of the atomic number of the rare earth, t decreases from 0.8847 (La) to 0.8655 (Lu). In fact, all $\text{ReBa}_2\text{Cu}_3\text{O}_y$ compounds are stable. Fig.3 shows the calculated tolerance factors, t , of $\text{Re}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$ with x . The Re123 structure can only exist in a certain region of Re^{3+} substitution for Ba^{2+} . The solubility of Re ions at the Ba-sites depends on the size of the rare earth ion. The bigger the rare earth ion, the larger its solubility is. La has the widest solubility at the Ba-sites ($x \leq 0.7$). Y has the narrowest solubility and $\text{YBa}_2\text{Cu}_3\text{O}_y$ is a point compound in the phase diagram. According to our calculated results, it is found that the solubility of rare earth ions at the Ba-sites can be scaled well by the tolerance factor. The $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$ solid solution has been studied extensively. The solubility of Nd is more reliable, which is $x=0.6$. If we use the tolerance factor of $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$ with $x=0.6$ as a criterion ($t_c=0.8583$). For $t > t_c$ the Re123 phase can be formed, whereas for $t < t_c$ the Re123 is unstable. Using this criterion, we can obtain the solubility of the rare earth ions at the Ba-sites of $\text{Re}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$ (see Fig.3). For La, Pr, Sm, Eu, Gd, the solubilities are 0.7, 0.69, 0.47, 0.42 and 0.38, respectively, which are very close to the experimental results [12-16]. The solubility of Nd in $\text{YBa}_{2-x}\text{Nd}_x\text{Cu}_3\text{O}_y$ is estimated to be $x=0.30$ by the above criterion, which is consistent with our experimental result.

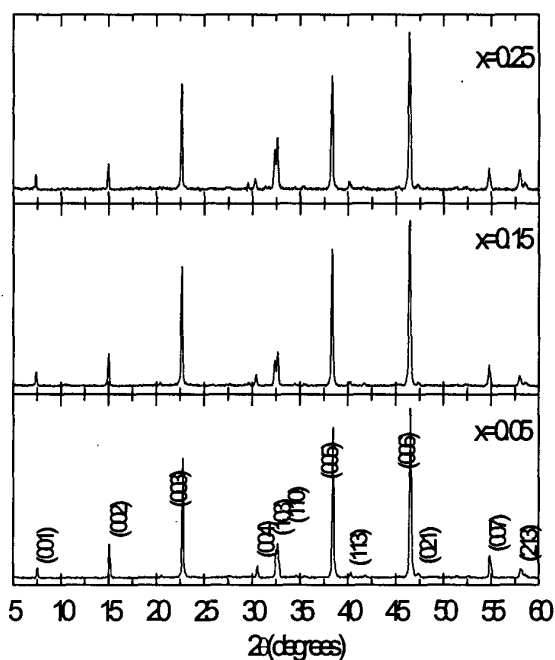


Fig. 1. X-ray diffraction patterns of $\text{YBa}_{2-x}\text{Nd}_x\text{Cu}_3\text{O}_y$

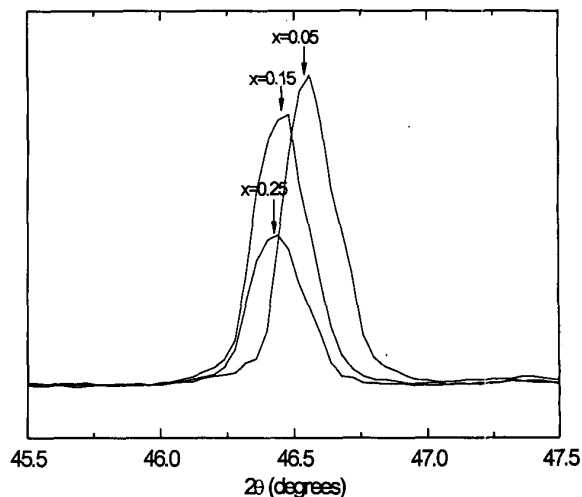


Fig. 2. X-ray diffraction peak profiles at $2\theta=46.5^\circ$

TABLE I
CALCULATED TOLERANCE FACTOR OF Re123 COMPOUNDS

Compound	Tolerance Factor	Compound	Tolerance Factor
$\text{YBa}_2\text{Cu}_3\text{O}_y$	0.8705	$\text{TbBa}_2\text{Cu}_3\text{O}_y$	0.8739
$\text{LaBa}_2\text{Cu}_3\text{O}_y$	0.8847	$\text{DyBa}_2\text{Cu}_3\text{O}_y$	0.8722
$\text{PrBa}_2\text{Cu}_3\text{O}_y$	0.8843	$\text{HoBa}_2\text{Cu}_3\text{O}_y$	0.8706
$\text{NdBa}_2\text{Cu}_3\text{O}_y$	0.8822	$\text{ErBa}_2\text{Cu}_3\text{O}_y$	0.8691
$\text{SmBa}_2\text{Cu}_3\text{O}_y$	0.8787	$\text{TmBa}_2\text{Cu}_3\text{O}_y$	0.8679
$\text{EuBa}_2\text{Cu}_3\text{O}_y$	0.8771	$\text{YbBa}_2\text{Cu}_3\text{O}_y$	0.8748
$\text{GdBa}_2\text{Cu}_3\text{O}_y$	0.8756	$\text{LuBa}_2\text{Cu}_3\text{O}_y$	0.8655

t was calculated according to the formula of $t = (r_{\text{Re}}/3 + 2r_{\text{Cu}}/3 + r_{\text{O}}) / \sqrt{2} (r_{\text{Ba}} + r_{\text{O}})$, r_{Re} , r_{Ba} , r_{Cu} and r_{O} are the radii of Re^{3+} , Ba^{2+} , Cu^{2+} and O^{2-} , respectively

It is found that the structural transition from orthorhombic to tetragonal is also related to the tolerance factor, t . For $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$, $\text{Sm}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$ and $\text{Eu}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$, with an increase in x , the structural transition from orthorhombic to tetragonal occurs at $x=0.2$, 0.1 , and 0.1 , respectively [16]. These x values correspond to almost the same tolerance factor ($t=0.8743$). This indicates that the structural transition occurs at a critical tolerance factor. The tolerance factor might be a characteristic parameter to describe the structural transition of the Re123 phase. For $\text{YBa}_{2-x}\text{Nd}_x\text{Cu}_3\text{O}_y$, it is found that the tolerance factors are smaller than 0.8743 in all investigated regions. The tetragonal Re123 structure is stable. Thus the structural transition from orthorhombic to tetragonal was not observed.

The superconducting temperature, T_c , was determined from the resistance and ac susceptibility curves. The results are summarized in Table II and Fig. 4. For $x < 0.4$, the onset temperature T_c^{on} is almost independent of the Nd content x , all are higher than 95K. The magnetic transition temperature T_c^{Z} and the zero resistance temperature T_c^{zero} , however, exhibit two obvious steps. The first step occurs in the region of $0 \leq x \leq 0.25$, and T_c^{zero} is above 92K. The highest T_c^{zero} is 94K for $x=0.25$. The second step is in the region of $0.3 \leq x \leq 0.40$; T_c^{zero} is about 84K. For $x=0.5$, T_c^{on} dropped sharply to 30K, and T_c^{zero} is below 10K.

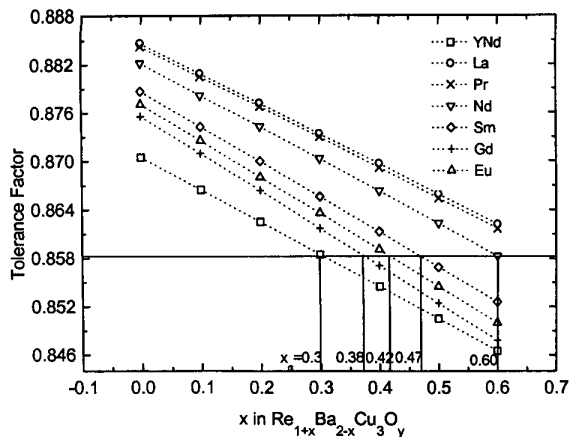


Fig. 3. Calculated tolerance factor of $\text{Re}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$

TABLE II
SUPERCONDUCTING TEMPERATURE OF $\text{YBa}_{2-x}\text{Nd}_x\text{Cu}_3\text{O}_y$

x	T_c^{on} (K)	T_c^{zero} (K)	T_c^* (K)
0.00	95.5	92.0	93.0
0.05	95.0	92.0	92.5
0.10	95.5	92.5	93.0
0.15	95.0	91.5	92.0
0.20	95.0	92.5	92.0
0.25	96.0	94.0	93.0
0.30	95.0	83.0	85.0
0.35	95.0	86.0	88.0
0.40	95.0	85.0	86.0
0.50	30.0	<10.0	

T_c^{on} is the onset transition temperature of the resistance curve;
 T_c^{zero} the zero resistance temperature;
 T_c^* the transition temperature of the ac susceptibility.

The substitution of Nd^{3+} for Ba^{2+} probably gives rise to three kinds of possible effects. The first one is the size effect from the difference of the radii of Nd^{3+} (0.995Å) and Ba^{2+} (1.34Å). It has little effect on the superconductivity, but has an obvious effect on the solubility of Nd at the Ba-sites and the structural transition from orthorhombic to tetragonal as discussed above. The second one is the magnetic pair breaking from the magnetic Nd^{3+} ions ($3.54\mu_B$) due to the spin-dependent exchange scattering of mobile holes in the CuO_2 planes by the magnetic Nd^{3+} ions at the Ba-sites. According to the theory of Abrikosov and Gor'kov, a linear suppression of T_c with the magnetic impurity concentration x would be expected. That does not agree with our experimental results. From the view point of the crystal structure, the rare earth and Ba sites originate from the same crystallographic sites of the disordered (Re,Ba) CuO_3 perovskite. In the ordered distorted perovskite Re123 structure, the distances from the Re- and Ba-sites to the CuO_2 plane are slightly different. It is well known that the magnetic interaction is strongly dependent on the interaction distance. In fact, the distance from Ba-sites to the CuO_2 plane is longer than that from Re-sites to CuO_2 plane. Thus the magnetic depairing effect from the magnetic Re ions at Ba-sites should be smaller than that at Re-sites. It is believed that magnetism of Re ions at Re-sites does not effect the superconductivity in

ReBCO superconductors. The third one is due to the difference in the valences of Nd^{3+} and Ba^{2+} . The superconductivity of p-type doped superconductors is dependent on the holes predominantly on the oxygen sites in the CuO_2 planes, and substitution of Re^{3+} for Ba^{2+} would require donor electrons, whence canceling partial holes on the CuO_2 planes. The superconducting transition temperature, T_c , should then decrease with increasing the content of Re^{3+} . Our results show that T_c is almost unchanged for $x \leq 0.25$. That might suggest that the charge balance is maintained by the extra oxygen and the total hole concentration should not change. Neutron diffraction indicates that the increase of Nd at the Ba-sites results in an increase of the occupation of the O_5 sites [9]. The O_5 does not affect the CuO_2 plane directly, but affects on the CuO_2 plane indirectly through O_4 . Due to the screening of O_4 it is possible for O_5 to not suppress the superconductivity in a certain occupation of O_5 . The superconducting transition temperatures T_c of $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$ solid solution, reported by different groups, seems very scattered [9][15-19]. Yossefov et al. reported that T_c was insensitive to Nd content, x , a ranged between 98.7 and 94K for $x < 0.25$ [19]. That is very similar to our result (See Fig.4). The scattered results for the T_c of $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$ solid solutions indicate that the oxygen content and the oxygen occupation are key factors for the superconductivity. We believe that the oxygen content and charge transfer due to the difference in the valences of Nd^{3+} and Ba^{2+} may be the key factor in the superconductivity of $\text{YBa}_{2-x}\text{Nd}_x\text{Cu}_3\text{O}_y$. The magnetic pair breaking of magnetic rare earth ions at the Ba-sites seems not to be a major factor in the T_c -depression of $\text{ReBa}_2\text{Cu}_3\text{O}_y$ superconductors. This was supported by our recent results on $\text{YBa}_{2-x}\text{Pr}_x\text{Cu}_3\text{O}_y$ [20].

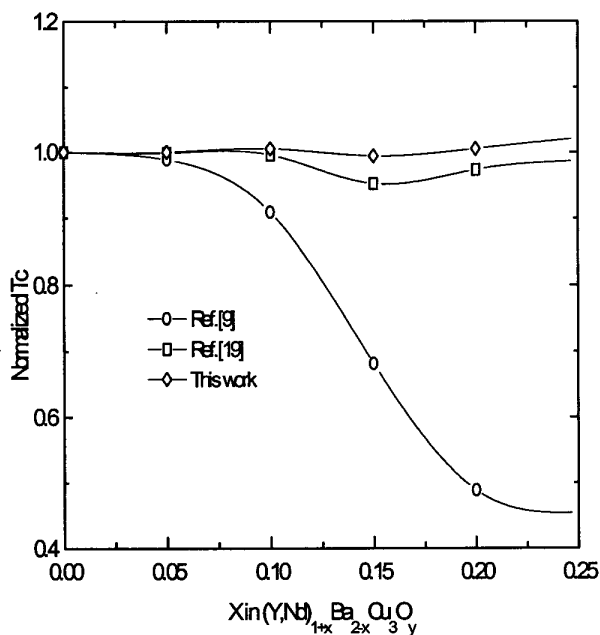


Fig. 4 Normalized T_c for $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$ and $\text{YBa}_{2-x}\text{Nd}_x\text{Cu}_3\text{O}_y$.

IV. CONCLUSIONS

The solubility of Nd on the Ba-sites in $\text{YBa}_{2-x}\text{Nd}_x\text{Cu}_3\text{O}_y$ was determined to be $x=0.25$ by x-ray powder diffraction. The solubility of Nd and the structural transition from orthorhombic to tetragonal are related to a geometric parameter, the tolerance factor, t . The onset superconducting transition temperature, T_c^{on} , determined from the curves of resistance vs temperature, exhibits a weak dependence on the Nd content, x , for $x < 0.4$. The variation in the zero resistance transition temperatures, T_c^{zero} , vs the Nd content, x , exhibits two steps. For $x \leq 0.25$ T_c^{zero} values are all above 92K, and $T_c^{\text{zero}}=94\text{K}$ for $x=0.25$. For $x \geq 0.3$ T_c^{zero} drops sharply to about 84K, and finally for $x=0.5$ T_c^{on} falls to 30K and T_c^{zero} is below 10K. The small compatibility of Nd and Ba in $\text{YBa}_2\text{Cu}_3\text{O}_y$ system does not seriously suppress the superconductivity. The oxygen content and charge transfer due to the unbalance between Nd^{3+} and Ba^{2+} might be key factors in the superconductivity of $\text{YBa}_{2-x}\text{Nd}_x\text{Cu}_3\text{O}_y$. The magnetic pair breaking of magnetic rare earth ions at the Ba-sites seems not to be a major factor in the T_c -depression of $\text{REBa}_2\text{Cu}_3\text{O}_y$ superconductors.

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