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Journal of Alloys and Compounds 408–412 (2006) 223–225

Journal of ALLOYS AND COMPOUNDS

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Internal friction and oxygen migration in $Nd_xY_{1-x}Ba_2CuO_y$ ($x = 0.0$–1.0) superconductors at low frequencies

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Available online 31 May 2005

Abstract

The internal friction and shear modulus of a series of $Nd_xY_{1-x}Ba_2Cu_3O_y$ ($x = 0.0$–1.0) superconductors were measured over the temperature range of 300–700 K at frequencies of 0.032–10.0 Hz using a forced torsional vibration method. Anelastic relaxation peaks due to oxygen migration were observed at temperatures from 410 to 520 K. The Arrhenius plots of logarithmic relaxation time versus inverse peak temperature for the internal friction peaks showed an unsystematic shift with an increase in the neodymium composition, while changes of the average cell structure exhibited a linear relationship when plotted versus the average ionic radius for trivalent rare earth ions with the coordination number eight.

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Keywords: $Nd_xY_{1-x}Ba_2Cu_3O_y$ superconductor; Oxygen migration; Anelastic relaxation; Internal friction; Rare earth substitution

1. Introduction

Internal friction measurement is a powerful tool for the investigation of defect dynamics in electrically conductive crystals. Several groups have performed anelastic measurements employing different techniques to investigate oxygen migration (and defects) in $YBa_2Cu_3O_y$ (Y123) [1–11] and $RBa_2Cu_3O_y$ (R123, R = rare earth) [12–15]. Oxygen migration behavior in R123 is considerably influenced by the ionic size of the rare earth ion [12–14]. Although the actual role of rare earth substitution in oxygen relaxation in R123 is still unclear, changes in atom position and the interlayer distances of the orthorhombic phase [16,17] may affect oxygen migration. Previously, we reported systematic results obtained in internal friction measurements of $Nd_xY_{1-x}Ba_2Cu_3O_y$ (NdY123, $x = 0.0$–1.0) [18]. The internal friction peak temperature measured at 200 kHz showed an unsystematic shift with an increase of x, while changes in the average cell structure exhibited a linear relationship when plotted versus the average ionic radius. In this earlier experiment, our measurements were conducted within a limited frequency region.

Here, we report the systematic results of anelastic measurements of NdY123 conducted over the frequency range of 0.032–10.0 Hz employing a forced torsional vibration method. This study provides confirmed results on the anelastic relaxation of NdY123 observed between the temperatures of 410 and 520 K, which is associated with oxygen migration. It is demonstrated that partial substitution by Y^{3+} ions on Nd sites significantly affects oxygen migration in NdY123.

2. Experimental

NdY123 powders were synthesized by solid-state reaction from Nd_2O_3 and Y_2O_3 (Shin-etsu Chemical Co., 99.9%), and $BaCO_3$ and CuO (Waco Chemical Co., 99.9%). Using a die press, we formed 4 mm × 30 mm × 0.5 mm bar of NdY123 at 100 MPa. All of the samples except for the Y123 were sintered at 1213 K for 15 h in flowing argon. This process conducted in reduced oxygen at partial pressure is essential to inhibit partial substitution on Ba sites by Nd^{3+} ions [19]. The Y123 specimens were sintered at 1193 K for 15 h in air.

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0925-8388/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2005.04.054

All of the sintered specimens were heated at 823 K for 15 h in flowing oxygen and then cooled in the furnace. The oxygen content of the samples was determined by themogravimetric (TG) measurement. Internal friction and shear modulus were measured at frequencies ranging from 0.032 to10.0 Hz using a forced torsional vibration method with a commercial apparatus (MR-500, Rheology Co., Ltd, Japan). The lattice parameters for the orthorhombic phases were determined by the least squares method using diffraction peaks.

3. Results and discussion

The lattice parameters and oxygen content obtained for our NdY123 specimens are summarized in Table 1. X-ray diffraction indicated the orthorhombic phase of NdY123. The unit-cell parameters increased with an increase in Nd composition, while the orthorhombicity decreased. The oxygen content of our NdY123 samples annealed in oxygen was determined to be 6.86 ± 0.04 or greater. The oxygen content of the NdY123 samples after internal friction measurement agreed with the starting composition within the error limits of the TG measurement.

In dynamic torsional-elasticity measurements conducted at 0.032–10 Hz, an internal friction peak appeared between 410 and 520 K depending upon the measurement frequency. This peak is associated with oxygen migration in the basal plane [1–15]. Fig. 1 shows the internal friction and shear modulus plotted against inverse temperature for a $Nd_{0.8}Y_{0.2}Ba_2Cu_3O_y$ sample.

We calculated the parameters of the internal friction peaks, i.e., peak temperature T_p, activation enthalpy H_a (the subscript “a” denotes the apparent value), and relaxation amplitude A as a single Debye peak, using Eq. (1) by applying the least-square fitting technique to the internal friction data:

$$Q^{-1} = \frac{A\tau\omega}{1+\tau^2\omega^2} \tag{1}$$

$$\tau = \tau_0 \exp\left(\frac{H}{kT}\right) \tag{2}$$

where τ is the relaxation time, ω the angular frequency ($\omega = 2\pi f_m$, f_m denotes the measurement frequency used in the experiment), H the activation enthalpy, τ_0 the pre-exponential factor, and k the Boltzmann’s constant. The fitting parameters for the NdY123 series measured at 0.32 Hz are summarized in Table 1.

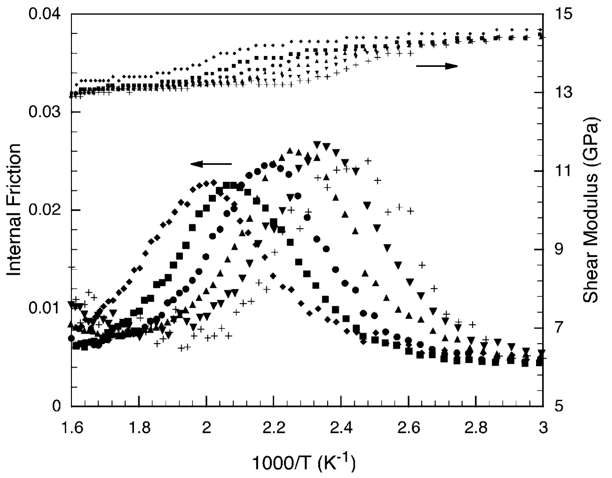

Fig. 1. Internal friction and shear modulus plotted against inverse temperature for $Nd_{0.8}Y_{0.2}Ba_2Cu_3O_y$ measured at 10.0 (◆), 3.2 (■), 1.0 (●), 0.32 (▲), 0.10 (▼) and 0.032 Hz (+).

Fig. 2 shows Arrhenius plots of the logarithmic relaxation time ($\log\tau$) versus the inverse peak temperature ($1/T_p$) for the internal friction peaks of our NdY123 samples. The activation enthalpy H and pre-exponential factor τ_0 calculated from the Arrhenius plots (Fig. 2) are summarized in Table 1. The activation enthalpy values calculated from the Arrhenius plots are roughly twice as large as the apparent activation enthalpy H_a calculated from the internal friction peaks for which a single Debye peak is assumed. It should be noted that the H value determined according to the Arrhenius law is averaged over a distribution of activation enthalpy depending on the local distribution of defect structures. Thus, the difference between H and H_a probably reflects a wide distribution of hopping oxygen ions – and, therefore, defects – in the local environment.

The unit-cell parameters of the NdY123 samples decreased with increasing Y^{3+} composition. The average cell structure exhibited a linear relationship when plotted versus the average ionic radius for trivalent rare earth ions with the coordination number eight [20]. Recently, Fita et al. re-

Table 1
Lattice parameter and oxygen content of $Nd_xY_{1-x}Ba_2Cu_3O_y$ specimens

Specimen	Lattice parameter (nm)			Oxygen content	T_p (K)	H_a (eV)	A	H (eV)	$\log\tau_0$
	a	b	c						
$NdBa_2Cu_3O_y$	0.3869	0.3921	1.1746	6.81 ± 0.04	434 ± 3	0.65	0.036	1.33	−15.8
$Nd_{0.8}Y_{0.2}Ba_2Cu_3O_y$	0.3859	0.3915	1.1737	6.82 ± 0.04	441 ± 3	0.59	0.043	1.17	−13.6
$Nd_{0.6}Y_{0.4}Ba_2Cu_3O_y$	0.3852	0.3909	1.1719	6.89 ± 0.04	430 ± 3	0.57	0.016	1.65	−19.6
$YBa_2Cu_3O_y$	0.3824	0.3892	1.1686	6.91 ± 0.04	464 ± 3	0.43	0.097	1.17	−13.0

Also shown fitted peak parameters (peak temperature T_p, activation enthalpy H_a and relaxation amplitude A) as a single Debye peak for the internal friction peak measured at 0.32 Hz. Activation enthalpy H and preexponential factor τ_0 determined from the Arrhenius plots.

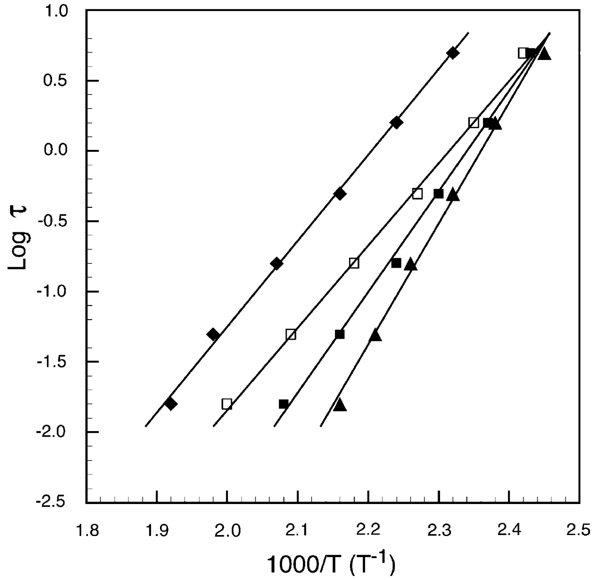

Fig. 2. Arrhenius plots of logarithmic relaxation time vs. inverse peak temperature for internal friction peaks of $NdBa_2Cu_3O_y$ (■), $Nd_{0.8}Y_{0.2}Ba_2Cu_3O_y$ (□), $Nd_{0.6}Y_{0.4}Ba_2Cu_3O_y$ (▲) and $YBa_2Cu_3O_y$ (♦).

ported that rare earth ion size affects the activation energy of oxygen hopping between O(1) and O(5) sites during the oxygen ordering process, and that this activation energy depends strongly on the unit-cell volume [21]. In our present work, however, no clear relationship between the activation enthalpy H and the unit-cell volume was observed. The log τ–1/T curves show an irregular shift with an increase in the Nd composition when $x = 0.6$ (Fig. 2). This unsystematic shift of the log τ–1/T curves indicates that oxygen relaxation in NdY123 is influenced by more than the average cell structure. It can be regarded that there is no direct interaction between the substituted Y^{3+} ions and the moving oxygen ions or defects, since the rare earth sites in NdY123 are remote from the sites of the oxygen ions or defects in the Cu–O plane. However, rare earth substitution affects both atom position and the interlayer distances of the orthorhombic phase [22,23]. Such influences on crystal structure have been reported for $Pr_{0.5}R_{0.5}Ba_2Cu_3O_y$ [23], $Y_{1-x}Pr_xBa_2Cu_3O_y$ [24], and $La_{0.5}R_{0.5}Ba_2Cu_3Oy$ compounds [25]. Phase separation due to strain relaxation at different interatomic distances has also been discussed in cases where there are large differences in rare earth size [25]. Thus, local distortion of the lattice due to a mismatch of the ionic radius between Nd^{3+} and Y^{3+}, and/or changes in the interatomic distances could occur in a NdY123 system. Such lattice distortion and/or changes in interatomic distances due to partial Y^{3+} substitution may account for changes in the distribution of relaxing oxygen ions in the local environment. Our present results suggest that oxygen hopping in a NdY123 system is influenced strongly by the distribution of local structures (i.e., defects) around the relaxing oxygen ions due to the indirect effects of partial rare earth substitution.

4. Conclusion

This work provides systematic data on internal friction for a series of $Nd_xY_{1-x}Ba_2Cu_3O_y$ ($x = 0.0$–1.0) (NdY123) superconductors over the frequency range of 0.03–10.0 Hz. Anelastic relaxation peaks due to oxygen migration in the NdY123 samples were observed between the temperatures of 410 and 520 K. The activation enthalpy obtained from log τ–1/T curves showed an unsystematic shift with an increase of x, while changes in the average cell structure exhibited a linear relationship when plotted versus the average ionic radius. This indicates that oxygen relaxation in NdY123 is influenced not only by the average cell structure, but also by the local environment (i.e., defects) around the relaxing oxygen ions which is altered by the co-doping of Nd and Y.

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