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Dynamic modulus relaxation of $ErBa_2Cu_3O_{6+x}$ near the orthorhombic to tetragonal phase transition at 200 kHz

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Abstract

The dynamic modulus and internal friction of $ErBa_2Cu_3O_{6+x}$ were measured at the temperatures from 300 to 1070 K using a $LiNbO_3$ composite oscillator technique at 200 kHz. An anelastic relaxation due to oxygen movement at 200 kHz was observed to be associated with the orthorhombic-to-tetragonal (O–T) phase transition in $ErBa_2Cu_3O_{6+x}$ at 850–900 K. We provided new data on the relaxation time and peak temperature in the highest frequency region by fitting for the measured internal friction against temperature. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Young's modulus; $ErBa_2Cu_3O_{6+x}$; Phase transition; Debye peak; Internal friction $LiNbO_3$ composite bar method

1. Introduction

The oxygen dynamics in electronic conducting crystals such as high-temperature superconducting oxides can be investigated by anelasiticity measurement over a wide-range frequency and temperature using various techniques. Here, we report the dynamic modulus and internal friction of $ErBa_2Cu_3O_{6+x}$ at 200 kHz by the mean of a $LiNbO_3$ composite oscillator that we have previously developed [1]. An oxygen relaxation affects both the dynamic modulus and phase transition of oxygen-defective oxide crystals. In this work, we will observe the anelastic relaxation, which is associated with the orthorhombic-to-tetragonal (O–T) phase transition of $ErBa_2Cu_3O_{6+x}$ by using a moderate frequency of 200 kHz. The data of relaxation time and temperature at the highest region of frequencies than any previous work for $ErBa_2Cu_3O_{6+x}$ is provided by this measurement. Also, the superimposing phenomenon between phase transition and oxygen relaxation will be discussed.

2. Experimental

The bars of $ErBa_2Cu_3O_{6+x}$ with 1 mm-diameter and ca.10 mm-length were fabricated by a ceramic extrusion technique described as in a previous study [2,16]. All the samples were polycrystalline bodies, followed by annealing treatment at 623 K in flowing oxygen. For the measurement, the sample bar was cemented with a 200 kHz–$LiNbO_3$ resonator at each end using inorganic bonding agent, and followed by heat-treatment at ca. 470 K. We confirmed that the bonding interface-layer was very thin so that it did not affect the measured data. The measurement was performed in the heating-cooling cycles with 2.5 K/min at the temperature range of 300–1070 K. Using the as-cemented composite-bar of a sample and an oscillator, we directly observed the effect of heat treatment in air on the elastic property of $ErBa_2Cu_3O_{6+x}$. The value x was monitored by thermo-gravity (TG) measurement before the elastic measurement. We used the mathematical relationship and calibration to get dynamic Young modulus E and internal friction, as discussed in previous works [3,4].

3. Results and discussion

Fig. 1 shows the plots of Young's modulus (along a long axis of a bar) and internal friction vs. temperature for an $ErBa_2Cu_3O_{6+x}$ sample bar, sintered at 1173 K and followed by heat treatment at 823 K in oxygen. The data were obtained at ca. 200 kHz with a heating rate of 2.5 K/min in air. The oxygen stoichiometry of the sample was measured as $x=0.1$. The sample attained the superconducting state below 90 K. An internal friction peak appears at around 880 K and the orthorhombic-to-tetragonal (O–T) transition at 913 K. The thermal expansion measurement

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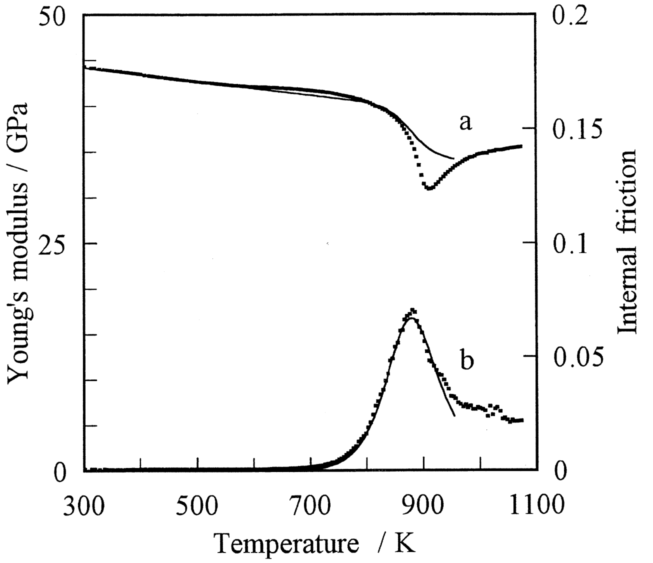

Fig. 1. Plots of (a) Young's modulus and (b) internal friction for $ErBa_2Cu_3O_{6+x}$ at 200 kHz (the first heating step). Solid lines represent Debye-type relaxation using the fitted parameters in Table 1.

with a heating rate of 5 K/min also indicated an anomaly at around 700 K–950 K. The coefficient was 1.25×10^{-5} K^{-1} for 300–690 K, 2.80×10^{-5} K^{-1} for 690–930 K, and 1.19×10^{-5} K^{-1} above 930 K. Here we assumed that the O–T phase transition temperature T_{O-T} was characterized by the minimum in modulus.

As expected for Debye-type behavior, the internal friction peak position shifted to lower temperature for the data measured at 0.1 Hz–10 Hz in our previous work [16]. On the other hand, The O–T phase transition temperature is almost the same for the data at different frequencies [16–18]. The change of modulus and internal friction vs. temperature seems to be complicated with superimposing phenomena due to the oxygen relaxation and the O–T phase transition. In the present case, internal friction peak is not fitted by a simple Debye peak against temperature T. A Debye-type modulus relaxation and internal friction are represented as

$$E = E_U/\{1 + A/(1 + \omega^2\tau^2)\} \qquad (1)$$

$$Q^{-1} = A\,\omega\tau/(1 + \omega^2\tau^2) \qquad (2)$$

$$\tau = \tau_0 \exp(H/kT) \qquad (3)$$

where E and E_U are total and unrelaxed modulus (reciprocal compliance along a long axis), Q^{-1} is internal friction, A is the relaxation amplitude, τ and τ_0 are the relaxation time and its pre-exponential term, respectively, and ω is angular frequency ($\omega = 2\pi f$), H is an activation enthalpy and k is the Boltzman constant. We determined the expected peak temperature of internal friction (relaxation) using Eqs. (2) and (3) by applying the least-square fitting technique to the internal friction data below the peak temperatures. The results of parameters fitted as single Debye peaks are summarized in Table 1. The fitted Debye behavior indicates the difference between the expected and observed lines for the modulus in Fig. 1, which was due to relaxation near O–T phase transition. The similar internal friction above room temperature for $YBa_2Cu_3O_{6+x}$ (YBCO) has been investigated [5–14]. Most of workers have discussed that this anelastic relaxation is due to oxygen movement between sites O(1) and O(5). In this work, we also conclude this relaxation as the phenomenon of oxygen movement between two oxygen sites in the crystal lattice of $ErBa_2Cu_3O_{6+x}$. Comparing with $YBa_2Cu_3O_{6+x}$, both the peak temperature of internal friction and the O–T phase transition were shifted to higher temperatures for $ErBa_2Cu_3O_{6+x}$.

Table 1
Data of fitted parameters for a single Debye peak; peak temperature T_p, relaxation time τ around peak temperature, relaxation amplitude A for internal friction, and O–T transition temperature T_{O-T} from the minimum for Young's modulus in $ErBa_2Cu_3O_{6+x}$

Heat cycle	T_p (K)	τ (sec)	A	T_{O-T} (K)
The first	880±5	7.7×10^{-7}	0.13±0.01	913±3
The third	875±5	7.7×10^{-7}	0.14±0.01	913±3

Fig. 2 illustrates the plots of Young's modulus and internal friction vs. temperature for the same sample of $ErBa_2Cu_3O_{6+x}$ in the third heating-up step. The fitted parameters for Debye-type behavior are summarized in Table 1 for two measurements. For the heat-treated $ErBa_2Cu_3O_{6+x}$, a slightly broader internal friction peak and corresponding drop of Young's modulus were observed. Since the concentration of oxygen vacancy can increase during multiple heating measurement at elevated

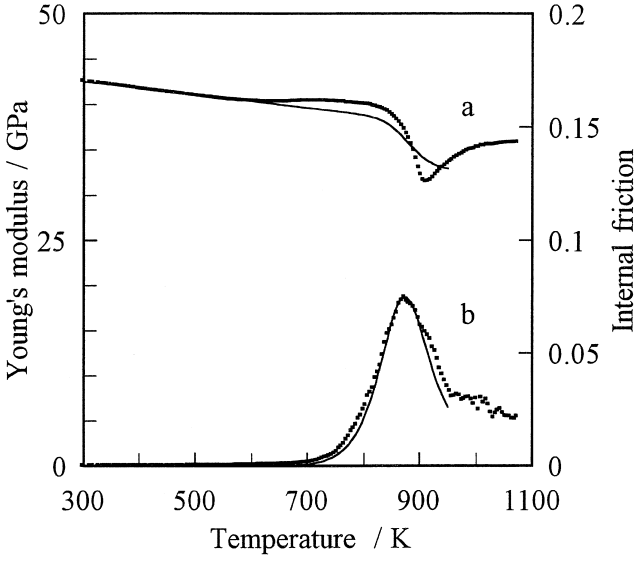

Fig. 2. Plots of (a) Young's modulus and (b) internal friction for $ErBa_2Cu_3O_{6+x}$ at 200 kHz in the third heating step. Solid lines represent Debye-type relaxation using the fitted parameters in Table 1.

temperatures, the distributed relaxation time or enthalpy should be induced. The increasing broadness is reasonable if the vacancy concentration become in equilibrium during heat treatment. On the other hand, we should note a small and broad peak for Young's modulus appeared below the temperature of the relaxation and O–T transition. The behavior is not interpreted by an ordinary relaxation form of Debye-type. In earlier research on modulus relaxation, Nowick and Berry [15] discussed a resonance-type relaxation for the elastic behavior of solids having dislocations. In their model, the relaxation should induce a resonance over the whole structure in a crystal. The mathematical representation is as following,

$$J^*/J_{\mathrm{U}} - 1 = A/\{1 - (\omega/\omega_0)^2 + i\ \omega\tau\} \tag{4}$$

where J^* is complex compliance, J_{U} is unrelaxed compliance part, ω_0 is a resonant frequency ($\omega_0^2 = J_{\mathrm{U}}/(Am_l)$) for mass, m_l introduced in a three element Voigt model. The resonance-type behavior is possible if $\omega_0\tau \ll 1$. The compliance (reciprocal Young's modulus in the present case) has the maximum and minimum values at around a frequency corresponding to a loss peak. However, the physical meaning for oxygen relaxation in a defective crystal seems to be uncertain, because no corresponding phenomenon has been actually observed so far. If oxygen relaxation occurred near a phase transition temperature (under an appropriate frequency), the movement of oxygen between equivalent sites might make an apparent mass in Voigt model, affecting the reconstruction of a softened lattice. It can be imagined that the compliance and loss change should be different from a simple or modified Debye-type behavior. The effect should be obvious if the vacancy concentration become rather large in the oxide (after heat treatment as in Fig. 2). In this work, although we do not conclude the resonance-type behavior can appear soon because of the weak feature (a very small and broad peak) in modulus before the O–T transition as in Fig. 1, they should be noted as a phenomenon worthy of study in more detail.

Among previous work on elastic property of YBCO-type superconductors above room temperature, only Tallon and coworkers [8,14] have applied the high frequency measurement (100 kHz-range) to $\mathrm{YBa_2Cu_3O_{6+x}}$ and $\mathrm{NdBa_2Cu_3O_{6+x}}$ using the Marx technique at these temperatures. They have described the interesting results being related to oxygen self-diffusion in the medium temperature-range. Their internal friction data have indicated a peak at 826 K at 40 kHz, however only a hint at 892 K at 144 kHz-measurement [8]. Since their plots are unfortunately sparse against temperature, it seems to be difficult to discuss toward detailed behavior on the combination of the O–T phase transition and oxygen relaxation in 100 kHz-range. Our measurements provide confirmation of the anelastic relaxation (both in modulus and internal friction) due to oxygen displacement between O(1)–O(5) sites near the O–T transition for polycrystalline $\mathrm{ErBa_2Cu_3O_{6+x}}$. This work has also discussed the data of the superimposing phenomenon between oxygen relaxation and phase transition.

4. Conclusion

We measured the dynamic Young's modulus and internal friction of $\mathrm{ErBa_2Cu_3O_{6+x}}$ at 200 kHz. The present data were a useful addition to the data on relaxation time and temperature in the highest frequency region for YBCO-type superconductors. Possible resonance-type relaxation was also discussed.

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References

[1] M. Ozawa, M. Inagaki, S. Suzuki, Rev. Sci. Instrum. 67 (1996) 2419.
[2] S. Suzuki, H. Kato, K. Iwashita, M. Takahashi, Jpn. J. Appl. Phys. 30 (1991) L991.
[3] H.M. Ledbetter, M. Lei, M.W. Austin, J. Appl. Phys. 59 (1986) 1972.
[4] S. Kudo, M. Ozawa, Jpn. J. Appl. Phys. 28 (Suppl. 2) (1989) 184.
[5] B.S. Berry, Bull. Am. Phys. Soc. 33 (1988) 512.
[6] X.M. Xie, T.G. Chen, Z.L. Wu, Phys. Rev. B 40 (1989) 4549.
[7] J.X. Zhang, G.M. Lin, Z.C. Lin, K.F. Liang, P.C.W. Fung, G.G. Siu, J. Phys.: Condens. Matter 1 (1989) 6939.
[8] J.L. Tallon, M.P. Staines, J. Appl. Phys. 68 (1990) 3998.
[9] J.R. Cost, J.T. Stanley, J. Mater. Res. 6 (1991) 232.
[10] G. Cannelli, R. Cantelli, F. Cordero, F. Trequattrini, M. Ferreti, Solid Stat. Comm. 82 (1992) 433.
[11] E. Bonetti, E.G. Campari, S. Mntovani, Physica C 196 (1992) 7.
[12] X. Woirgard, P. Gadaud, A. Rivière, B. Kaya, Mater. Sci. Forum 119 (1993) 719.
[13] J.L. Roubort, S.J. Rothman, J. Appl. Phys. 76 (1994) 5615.
[14] J.L. Tallon, B.-E. Mellander, Science 258 (1992) 781.
[15] A.S. Nowick, B.S. Berry (Eds.), Anelastic Relaxation in Crystalline Solids, Academic Press, NY, 1972, p. 614.
[16] M. Inagaki, M. Ozawa, S. Suzuki, Zairyou 47 (1998) 550.
[17] M. Ozawa, M. Inagaki, S. Suzuki, Jpn. J. Appl. Phys. 35 (1996) L1351.
[18] M. Ozawa, M. Inagaki, S. Suzuki, J. Electron. Mater. 28 (1999) 1032.