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Study of dielectric relaxation behavior in Nd_2CuO_4

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Abstract

The dielectric properties of the helium reduced Nd_2CuO_4 samples were studied by means of capacitance C and dissipation factor $\tan \delta$ measurements with the test frequency f in the range from 20 Hz to 1 MHz and at temperature T between 5 K and 325 K. In addition to obtain high dielectric constant at room temperature and low frequencies, two frequency-dependent peaks in the $\tan \delta$ curves and corresponding features in the real part dielectric constant ϵ' curves were observed near 118 K and 255 K for $f = 100$ Hz. The peak temperatures observed in the $\tan \delta$ curves at various test frequency f follow the relation $f = f_c e^{-W/kT}$, with $f_c = 3.1 \times 10^{13}$ (2.8×10^{14}) Hz and the activation energy $W = 0.282$ (0.60) eV for the 118 K (255 K) peak for the sample annealed at 880°C. The low temperature activation is attributed to the excitations from the ground state of $^4I_{9/2}$ multiplets to the first excited states of the $^4I_{11/2}$ multiplets. This assignment is further confirmed by the fact that the activation energy is reduced to 0.245 eV for the sample reduced at 920°C. The high temperature activation is related to the intrinsic excitations of the CuO_2 layers, and its activation energy is unaffected by the reduction temperatures used in this study. Our results indicate that reducing treatment produces the effect of increasing oxygen vacancies, probably through the removal of the O(2)'s (i.e., oxygens inbetween the Nd layers) in Nd_2CuO_4 . © 1997 Elsevier Science B.V.

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Nd_2CuO_4 has attracted a lot of research interest since the discovery of the electron-doped superconductivity in $R_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ ($R = \text{Pr}, \text{Nd}, \text{Sm}, \text{and Eu}$) [1,2] and $R_{2-x}\text{Th}_x\text{CuO}_{4-y}$ ($R = \text{Pr}, \text{Nd}, \text{and Sm}$) [2–4] with a superconducting transition temperature up to 24 K. This compound exhibits several magnetic transitions below room temperature in association with the antiferromagnetic ordering of the

Cu spins [5–9] or the Nd^{3+} ions [10–12]. In addition, magnetic susceptibility studies on single crystals of $\text{Nd}_2\text{CuO}_{4-y}$ reveal anisotropic characteristic with the easy axis of magnetization parallel to the basal plane below $T \approx 100$ K [13,14]. Although the above mentioned magnetic transition temperatures in $\text{Nd}_2\text{CuO}_{4-y}$ are not related to the oxygen deficiency in the samples [9,11], it has been shown that reduce treatment does reveal pronounced effects in the room temperature resistivity, optical reflectivity and transmission spectra [15], Raman spectra [16], and inelastic neutron scattering [17] data. Unlike other high- T_c

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oxides, the oxygen stoichiometry and the effect of reduce treatment remain controversial [18–22] for $\text{Nd}_2\text{CuO}_{4-y}$. Recently, Jandl et al. [23] studied the intermultiplet crystal-field excitations in $\text{Nd}_2\text{CuO}_{4-y}$ extensively using the Raman scattering and conjectured that the effect of reduction is to remove the extra apical oxygens O(3)'s in the sample. According to their result, reduce treatment will decrease the amount of the carrier concentration in the sample and increases the resistivity instead of decrease the room temperature resistivity by one order of magnitude [15]. Therefore, a comparison of the transport behaviors for $\text{Nd}_2\text{CuO}_{4-y}$ under different treatment conditions is still necessary.

Recently, measurements of the dielectric properties of the insulating phases of $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ [24,25], $\text{PrBa}_2\text{Cu}_3\text{O}_7$ [26], and La_2CuO_4 [27] revealed a high dielectric constant ($\epsilon' > 10^3$) at room temperature and low frequencies. This ferroelectric-like polarization is closely related to the antiferromagnetic ordering of the Cu moments within the Cu–O planes and chains of the samples and was suggested to be a common feature of the high- T_c oxides. Since Nd_2CuO_4 also contains CuO_2 layers and the Cu spins order antiferromagnetically at $T_N \approx 250$ K [5–9]. It is interesting to see whether such ferroelectric like behavior also exists in this system. Moreover, since the dielectric properties are very sensitive to the local electric field distribution within the samples, studies of the temperature and frequency dependences of the dielectric behaviors of Nd_2CuO_4 can reveal useful information about the defect concentration and provide us with better insight about the effect of reduce treatment in this compound. Such information will be useful for understanding why it is necessary for reduce treatment to produce superconductivity in $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$. We have studied the dielectric properties on the He-reduced $\text{Nd}_2\text{CuO}_{4-y}$ samples in temperatures between 5 K and 325 K with test frequencies in the range from 20 Hz to 1 MHz.

The samples used in this study were prepared by solid-state reaction from high purity Nd_2O_3 and CuO powders. Stoichiometric mixtures of these powders were ground thoroughly and heated in air at 900°C for 1 day and furnace cooled to room temperature. The resulting powders were pressed into pellets and fired in air at 900°C for another day and cooled to

room temperature. According to Tarascon et al. [10], reduce treatment above 900°C is essential for the occurrence of superconductivity and complete oxygen removal in $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$. Because we are interested in the effect of reduce treatment on the removal of the oxygens, we sintered the pellets in flowing He at 880°C and 920°C , respectively, for comparison in this study. Powder X-ray diffraction data reveal no impurity phase in the samples. Because the reported amount of oxygen removal is small (0.01–0.04 per unit cell) and the possibility of oxygen inhomogeneity in this compound, we did not make an effort to determine the oxygen content of the samples. The capacitance C and dissipation factor $\tan \delta$ measurements were performed on the disk-shaped pellets with silver paint coated on two sides of the pellets as the electrodes using a HP 4284A LCR meter in a He-dewar with a Si-diode as the temperature thermometer. The radius R of the pellets is 0.5 cm and the thickness d is of 0.1 cm. The real part dielectric constant ϵ' can be determined from the value of C through $\epsilon' = C/C_0$ where C_0 is $\epsilon_0 Ab/d$ with A being the area of the surface of the disk ($A = \pi R^2$) and b being the correction factor which has a value of 1.286 in our case.

The real part dielectric constant ϵ' as a function of temperature T curves with selected test frequencies f for Nd_2CuO_4 annealed at $T_a = 920^\circ\text{C}$ are plotted in Fig. 1(a). These ϵ' curves show distinct behaviors in different temperature regions. At the lowest temperatures, ϵ' is almost temperature and frequency independent and approaches a value of ≈ 8.4 at $T = 4$ K. With increasing temperature T , ϵ' increases and frequency dispersion develops. For $T \leq 60$ K, ϵ' exhibits a behavior characteristic of normal dielectrics and increases slightly with increasing T . The effect of test frequency on the ϵ' curves is weak in this temperature regime. For $T \geq 120$ K, the effects of temperature and frequency on ϵ' become more pronounced and ϵ' starts to increase rapidly with increasing T and decreases dramatically as the test frequency increases. Finally, an inflection in ϵ' appears at approximately 255 K, near the temperature T_N where antiferromagnetic ordering occurs in this system. The obtained value of ϵ' at room temperature is about 10^4 , a value that is comparable to that have been reported for other high- T_c oxides [24–27]. The ϵ' curves for the sam-

ple annealed at 880°C, with the same selected test frequencies, are plotted in Fig. 1(b). Although similar temperature and frequency characteristics were observed, it is interesting to notice that the effects of temperature and test frequency on ϵ' are even weaker for $T \leq 60$ K and the value of ϵ' at room temperature is smaller.

The fact that ϵ' becomes independent of frequency at lowest temperatures indicates that the observed response represents the static dielectric response of this system in the absence of dipolar effects. The slight increase of ϵ' with increasing temperature for $T \leq 60$ K may result primarily from the increase in the lattice polarizability or softening

Fig. 1. The logarithm of the real part dielectric constant $\log \epsilon'$ as a function of temperature T curves with selected test frequencies for the Nd_2CuO_4 sample annealed at (a) 920°C and (b) 880°C.

Fig. 2. The dissipation factor $\tan \delta$ versus temperature T curves with selected test frequencies for the Nd_2CuO_4 sample annealed at (a) 920°C and (b) 880°C.

of the lattice with increasing T . The rapid increase of ϵ' with increasing T and strong frequency dispersion in ϵ' observed for $T \geq 120$ K reveals characteristic of dipolar effects that are controlled by the activation of defects or localized charge centers in the samples. Such localized charge carriers are believed to be prevalent in the insulating phases of the high- T_c oxides. The smaller value of ϵ' observed at room temperature for the sample annealed with lower T_a indicates that the carrier concentration is smaller for that sample.

Shown in Fig. 2(a) are the dissipation factor $\tan \delta$ versus temperature T curves for selected values of f for the sample annealed with $T_a = 920^\circ\text{C}$. At low

temperatures, the observed value of $\tan \delta$ is quite small (< 0.005) and $\tan \delta$ increases slightly with increasing T for $T \leq 60$ K. Above 60 K, $\tan \delta$ increases substantially with increasing T with a peak occurring near 120 K. This peak temperature T_0 increases monotonically with increasing test frequency from 118 K for $f = 100$ Hz to ≈ 193 K for $f = 1$ MHz. Above 120 K, $\tan \delta$ exhibits characteristics similar to that of ϵ' and another peak occurs near 255 K for $f = 100$ Hz. This peak temperature T_1 is closely related to the inflection temperatures observed in the ϵ' curves and also increases monotonically with f to a value of ≈ 320 K for $f = 100$ kHz. Above 100 kHz, no maximum was observed in the $\tan \delta$ curves below the maximum temperature (325 K) measured. The rapid increase of $\tan \delta$ for $T > T_1$ indicates that dc effect becomes important above this temperature. For the sample annealed at 880°C , the $\tan \delta$ curves (shown in Fig. 2(b)) exhibit characteristics similar to that of the 920°C annealed sample. However, the value of T_0 at $f = 100$ Hz is higher (122.5 K) and the effect of test frequency on T_0 becomes weaker ($T_0 = 190$ K for $f = 1$ MHz) for the sample annealed at 880°C . The extra pronounced frequency dependent features in the $\tan \delta$ curves observed between T_0 and T_1 for the sample annealed at 880°C may indicate oxygen inhomogeneity in that sample.

For a Debye-type dielectric relaxation process the dissipation factor $\tan \delta = \chi''(\omega)/(1 + \chi'(\omega)) = (2 - \omega^2\tau^2)/(2 + \omega^2\tau^2)$ (where $\chi'(\omega)$ and $\chi''(\omega)$ are the real part and imaginary part of the dielectric susceptibility, respectively) and exhibits a peak for $\omega\tau = \sqrt{2}$. In order to see the temperature dependence of the peak position, the logarithm of the test frequency $\ln f$ versus the reciprocal of the peak temperatures (T_0 values and T_1 values) at the corresponding test frequency, $1000/T$, are plotted in Fig. 3(a) and (b). The observed linear relations between $\ln f$ and $1000/T$ for both peak temperatures indicate that the relaxation behaviors are thermally activated. From the deduced relation $f = f_c e^{-W/k_B T}$, we obtain $f_c = 3.1 \times 10^{13}$ (2.1×10^{12}) Hz and the activation energy $W = 0.282$ (0.245) eV for the low temperature peaks (T_0 values) for the sample annealed at 880°C (920°C), respectively. For the high temperature peaks (T_1 values), both f_c and the activation energy W are not affected by the annealing tempera-

Fig. 3. The natural logarithm of the test frequency $\ln f$ versus the reciprocal of the peak temperatures in the $\tan \delta$ curves (T_0 values for (a) and T_1 values for (b)) at the corresponding test frequency, $1000/T$, for the Nd_2CuO_4 samples annealed at 920°C and 880°C . The solid lines are least square fits for the data.

tures and we have $f_c = 2.8 \times 10^{14}$ Hz and $W = 0.60$ eV for both samples. Comparing with the existing data, it is interesting that our values of W for the low temperature peaks are related to that of the low energy peaks in the mid-infrared data [28] and are close to the two peaks' values (0.247 eV and 0.298 eV) as revealed from the inelastic-neutron-scattering [17] and Raman scattering [23] data for the excitations from the ground state of $^4I_{9/2}$ multiplets to the first excited states of the $^4I_{11/2}$ multiplets in Nd_2CuO_4 . Therefore, we believe that the excitation for the low temperature peaks is of the same origin.

Moreover, the lower value of the activation energy W for the sample with higher annealing temperature T_a indicates that it is the oxygen deficiency that is responsible for the relaxation behavior observed here. Since with higher reduction temperature, more oxygen vacancies will be removed from the sample which in turn produces more carriers in the sample that occupy the excited levels of the ground state multiplets. As a result, we have an excitation energy for the sample annealed at 920°C corresponding to the lower value (0.247 eV) of the doublet as observed from the inelastic-neutron-scattering and Raman scattering data. The smaller value of W (compared with 0.298 eV) for the sample annealed with $T_a = 880^\circ\text{C}$ indicates that the oxygen removal is not complete at that temperature.

Mid-infrared absorption data for the undoped lamellar copper oxides revealed an universal optical excitation near 0.5 eV which indicates that this absorption is from the intrinsic excitations of the CuO_2 layers [28]. From the obtained value of W (0.60 eV) and the peak temperature in the $\tan \delta$ curve (for $f = 100$ Hz), we believe that the excitation for the high temperature peaks is from the CuO_2 layers. Since reduce treatment at different temperatures (880°C and 920°C) produces no effect on the value of W , it is reasonable to conjecture that the oxygen vacancies are not in the CuO_2 layers (i.e., O(1) as shown in Ref. [23]). Instead, it is probably the oxygens inbetween the Nd layers (i.e., O(2)'s) that were removed after reduction.

In summary, we have studied the temperature and frequency dependences of the dielectric behaviors of Nd_2CuO_4 samples reduced at different temperatures. In addition to obtain high dielectric constant at room temperature and low frequencies, we also observed two thermally activated relaxations near 118 K and 255 K with the activation energy W of 0.282 (0.245) eV and 0.60 eV, respectively. The low temperature activation corresponds to the excitations from the ground state of $^4\text{I}_{9/2}$ multiplets to the first excited states of the $^4\text{I}_{11/2}$ multiplets and W is reduced with higher reduction temperature. The high temperature activation is related to the intrinsic excitations of the CuO_2 layers, and its activation energy is unaffected by the reduction temperatures used in this study. From this, we conjecture that reducing treatment produces the effect of increasing oxygen vacancies,

probably through the removal of the oxygens inbetween the Nd layers in Nd_2CuO_4 .

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