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# Mechanical spectrum and oxygen vacancies in γ-$Na_{0.66}CoO_2$

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ABSTRACT

The mechanical spectrum of γ-$Na_{0.66}CoO_2$ below room temperature was measured using the vibrating reed method at kilohertz frequencies. In the cooling process, internal friction is less temperature dependent above 240 K and shows a continuous decrease with the decrease in temperature below 240 K in annealed γ-$Na_{0.66}CoO_2$ sample. A transition was suggested to occur around 240 K, which is proposed to be a freezing transition of the mobility of sodium atoms. A similar behavior was observed in as-prepared γ-$Na_{0.66}CoO_2$ sample. However, another internal friction peak appears around 160 K. This internal friction peak is expected to be a thermally activated relaxation peak with some relationship to oxygen vacancies.



## 1. Introduction

Layered $Na_xCoO_2$ materials have been extensively investigated due to the recent discovery of high thermoelectric power and low in-plane resistivity in metallic $Na_{0.7}CoO_2$ [1], a charge ordered insulating state in $Na_{0.5}CoO_2$ [2], and superconductivity in the hydrated $Na_{0.35}CoO_2$ compound [3]. These electronic phases occur in the context of changes in the crystal structure. In $Na_xCoO_2$ system, the concentration of sodium affects the actual valence of Co and possible sodium ordering further impacts on the electronic and magnetic properties. Then many experimental or theoretical researches were performed on the issue of sodium ordering [4–19] and phase separation of sodium vacancies [20] in $Na_xCoO_2$ system.

Mechanical spectrum is a well-known probe for the study of the phase transition and the relaxation of micro-units such as point defects, dislocations, grain boundaries, and domain walls in solids [21–26]. It is sensitive to the mobility of atoms on an atomic scale. In previous research, a step increase of resonance frequency around 427 K with the decrease in temperature was observed in $Na_{0.66}CoO_2$ annealed at 400 °C in the flowing oxygen gas in the first flexural vibration mode [18]. This step increase does not show a clear shift in the mechanical spectrum measured at higher resonance frequency in the second flexural vibration mode. At the same time, the internal friction shows a continuous decrease below 427 K. The mechanical spectrum is much similar to that observed in a second-order atomic order–disorder phase transition [27]. A sodium ordering transition is proposed [18], which is also suggested by Raman spectroscopy [28]. Soon after, mechanical spectrum experiment was performed on as-prepared γ-$Na_{0.66}CoO_2$ sample. It suggests that oxygen deficiency emerges in as-prepared γ-$Na_{0.66}CoO_2$, which shifts the sodium ordering phase transition towards a lower temperature [19]. In this report, mechanical spectrum below room temperature is provided in both as-prepared and annealed γ-$Na_{0.66}CoO_2$ polycrystalline samples. The results seem to be consistent to the previous suggestion on oxygen deficiencies in our samples. At the same time, it implicates another freezing transition of the mobility of sodium atoms around 240 K by the temperature dependent internal friction.

## 2. Experimental

$Na_{0.66}CoO_2$ polycrystalline samples were synthesized by a solid-state reaction method following the "rapid heat-up" technique [18,29]. The starting material is a mixture of $Co_3O_4$ and $Na_2CO_3$ with some excess $Na_2CO_3$ due to Na evaporation during sample firing. The powder mixture is directly placed in a furnace preheated at 850 °C, lasting for 10 h and then slowly cooled down with a rate about 50 °C/h in atmosphere. Due to the fact that the sample is stable once the γ-$Na_{0.66}CoO_2$ phase is formed, the second sintering process follows the conventional heating route and the calcination condition is 850 °C for 10 h in atmosphere. The powders were pressed into rectangular bars before the second sintering process. Some of above as-prepared samples were further annealed at 400 °C for 24 h in the flowing oxygen gas, which is labeled as "annealed sample". The as-prepared and annealed samples were checked to be single-phased without impurity phase CoO and $Co_3O_4$ by room temperature powder X-ray diffraction using Cu Kα radiation.

The mechanical spectrum was measured for rectangular bars (40 mm × 4 mm × 0.3 mm) in the free–free flexural vibration mode from room temperature to liquid nitrogen temperature in the resonance frequency about several kilohertz both on the cooling and heating routes. A combination of electrostatic

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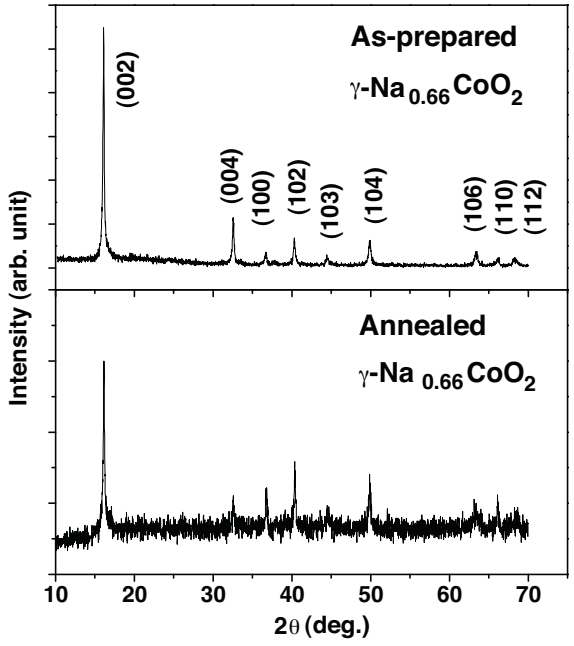


**Fig. 1.** Room temperature powder X-ray diffraction pattern of as-prepared and annealed $Na_{0.66}CoO_2$ samples.

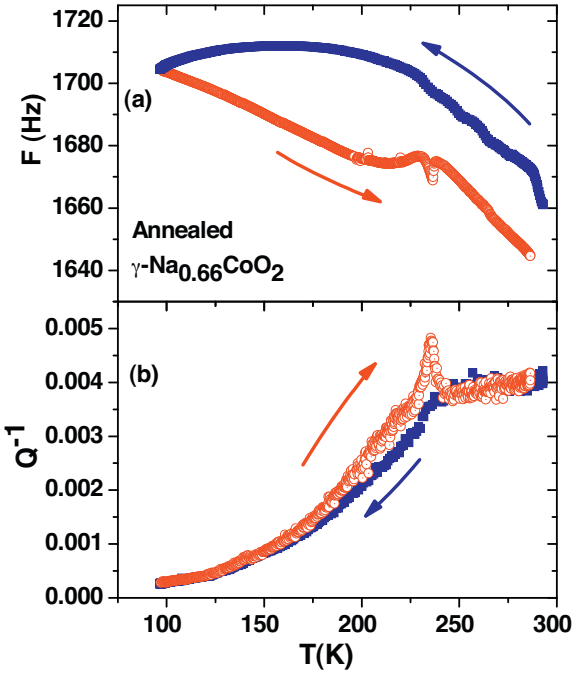


**Fig. 2.** Temperature dependent resonance frequency (a) and internal friction $Q^{-1}$ (b) measured on cooling and subsequent heating routes in annealed γ-$Na_{0.66}CoO_2$ sample (square in the cooling process and circle in the heating process).

drive and capacitor microphone detection was used with the details described in Ref. [22]. The experiments were conducted on cooling at a rate of about 2 K/min and on heating at about 1 K/min.

## 3. Results and discussions

Fig. 1 shows the room temperature powder X-ray diffraction pattern of our samples. No clear difference appears between powder X-ray diffraction pattern of as-prepared sample and that of annealed one. All diffraction peaks can be indexed in the hexagonal γ-$Na_xCoO_2$ phase with the lattice parameter $c = 10.97$ Å. The actual sodium content is thus expected to be 0.66 by comparison of the lattice parameter of $c$-axis with that reported in Ref. [6].

Fig. 2 represents the temperature dependent resonance frequency (Fig. 2a, Young's modulus is proportional to the square of resonance frequency ($Y \propto f^2$) and internal friction $Q^{-1}$ (Fig. 2b) measured on cooling and subsequent heating routes in annealed γ-$Na_{0.66}CoO_2$ sample. In the cooling process, internal friction is less temperature dependent above 240 K and shows a continuous decrease with the decrease in temperature below 240 K. A transition is suggested to occur around 240 K. In the heating process, similar mechanical spectrum was observed except a spike around 235 K. This spike is reproduced in several cooling/heating cycles and this feature might be due to thermal hysteresis of the transition. The thermal hysteresis is also observed in the temperature dependent resonance frequency on cooling and subsequent heating routes.

As we know, internal friction is sensitive to the mobility of atoms. In γ-$Na_xCoO_2$ sample, sodium atoms possess high mobility. Then it is expected the main contribution of internal friction at room temperature is related to sodium ion diffusion. Below 240 K, the internal friction shows a continuous decrease with the decrease in temperature, which might indicate a freezing transition of the mobility of sodium atoms. In previous $^{23}Na$ NMR study, a freezing transition of the mobility of sodium atoms above 200 K has been reported in γ-$Na_{0.8}CoO_2$ sample [30]. Since a sodium ordering transition is suggested to take place at higher temperature [19], the freezing transition might be due to a small portion of disordered sodium atoms.

Fig. 3 represents the temperature dependent internal friction $Q^{-1}$ (Fig. 3b) and resonance frequency (Fig. 3a) measured on cooling and subsequent heating routes in as-prepared γ-$Na_{0.66}CoO_2$ sample. In the cooling process, the internal friction below 250 K is similar to that in annealed sample except that another internal friction peak is superposed around 160 K. In the heating process, a continuous decrease of internal friction with the decrease in temperature below 240 K can be well discerned. The internal friction in

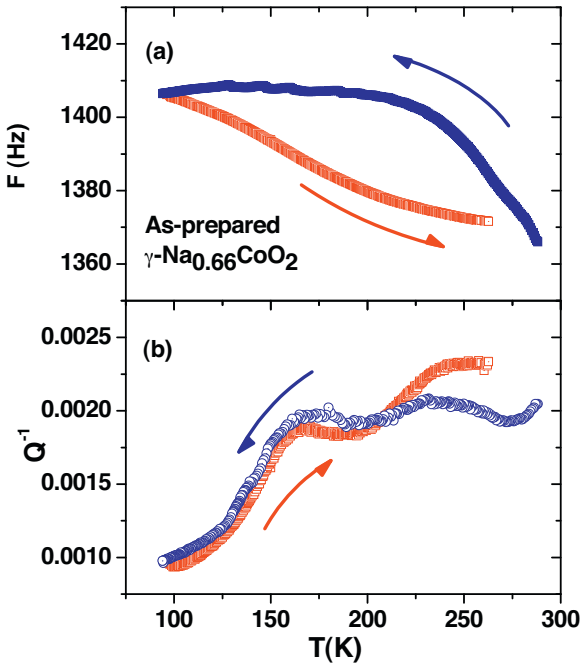


**Fig. 3.** Temperature dependent resonance frequency (a) and internal friction $Q^{-1}$ (b) measured on cooling and subsequent heating routes in as-prepared γ-$Na_{0.66}CoO_2$ sample (square in the cooling process and circle in the heating process).

the cooling process shows a bit difference compared with that on the heating route, where a small dip was observed around 273 K. The reason for the occurrence of this dip is not clear now and it will not be touched further. The overall internal friction above 240 K is larger in the heating than that in the cooling. This might be due to another kind of thermal hysteresis of the freezing transition. The temperature dependent internal friction also suggests a freezing transition of the mobility of sodium atomics in as-prepared γ-$Na_{0.66}CoO_2$ sample. At the same time, the thermal hysteresis is observed in the temperature dependent resonance frequency on cooling and subsequent heating routes, which is similar to that in annealed γ-$Na_{0.66}CoO_2$ sample.

In previous massive experimental studies, stoichiometric oxygen content is usually assumed. This is used to get the primary knowledge of the formal charge in the $CoO_2$ layers. The formal Co oxidation state is determined by the Na concentration and the charge neutrality in $Na_xCoO_{2-\delta}$ where oxygen content is expected perfectly to be 2. To investigate the oxygen nonstoichiometry parameter $\delta$, wet-chemical redox analysis is performed in a series of $Na_xCoO_{2-\delta}$ samples with the Na content $x$ ranging from 0.78 down to 0.12 [31]. The marked oxygen nonstoichiometry is observed for the low Na content sample. However, the oxygen is found to be stoichiometric to a precision of 1–2% by the Rietveld refinement of powder neutron diffraction of $Na_{0.74}CoO_2$ and $Na_{0.38}CoO_2$ at room temperature [32].

In previous high temperature mechanical spectrum study, a step increase of modulus and continuous decrease of internal friction with the decrease in temperature was observed around 427 K in annealed $Na_{0.66}CoO_2$. However, high temperature mechanical spectrum shows a large difference in as-prepared $Na_{0.66}CoO_2$ sample. The step increase of modulus with the decrease in temperature was shifted towards 345 K. As already shown in Fig. 1, no clear structural difference between as-prepared and annealed samples is found in the XRD pattern. And as-prepared oxide sample usually possesses lower oxygen concentration than that annealed in the flowing oxygen gas. Oxygen vacancy is suggested to emerge in as-prepared γ-$Na_{0.66}CoO_2$ and be absent in annealed γ-$Na_{0.66}CoO_2$ [19]. And it is oxygen vacancy that results in the different mechanical spectrum in as-prepared $Na_{0.66}CoO_2$ sample.

In line with above discussions, the internal friction peak around 160 K in as-prepared γ-$Na_{0.66}CoO_2$ also seems to relate to the oxygen vacancy. This peak does not show off a clear thermal hysteresis, which is consistent with the anelastic relaxation. Although the anelastic relaxation should be verified by the variation of peak position with the measured frequency, the internal friction peak around 160 K in as-prepared γ-$Na_{0.66}CoO_2$ sample, as we thought, tends much to be the anelastic one. The view is also supported by the comparison of temperature dependent reduce modulus $(\Delta Y/Y_0 = (Y - Y_0)/Y_0 \propto (f^2 - f_0{}^2)/f_0{}^2)$ in as-prepared and annealed samples on the heating route. The reduce modulus in annealed γ-$Na_{0.66}CoO_2$ on the heating route is shown in Fig. 4a, which can be fitted by a line. A deviation of the temperature dependent reduced modulus in as-prepared γ-$Na_{0.66}CoO_2$ from above linear behavior around 160 K is observed in Fig. 4a which is concurrent with the internal friction peak. This feature is consistent with the interpretation of the anelastic relaxation mechanism of internal friction peak around 160 K.

The internal friction peak in as-prepared γ-$Na_{0.66}CoO_2$ on the heating route is further tried to be analysed in terms of a single-time Debye relaxation being

$$Q_D^{-1} = \frac{T_M Q_M^{-1}}{T} \cdot \frac{2 \cdot 2\pi f\tau}{1 + (2\pi f\tau)^2} = \frac{T_M Q_M^{-1}}{T} \cdot \mathrm{sech}\left(\frac{E}{k_B} \cdot \left(\frac{1}{T} - \frac{1}{T_M}\right)\right) \quad (1)$$

$$\tau(T) = \tau_0 \cdot \exp\left(\frac{E}{k_B T}\right) \quad (2)$$

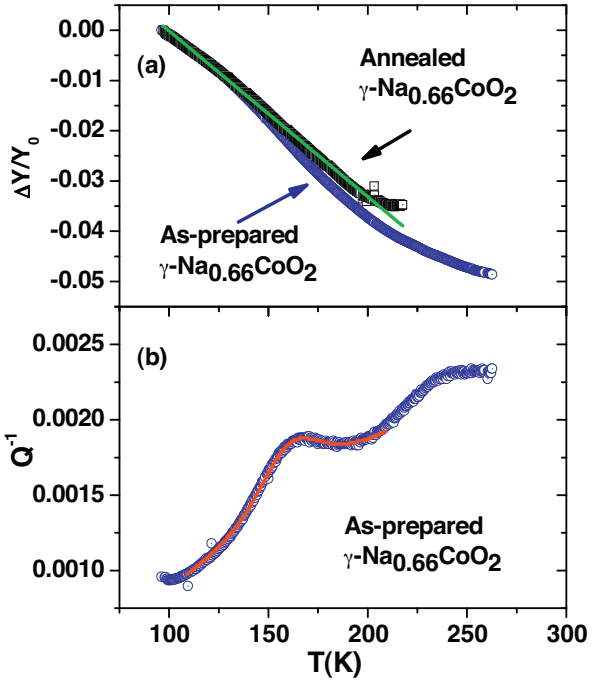


**Fig. 4.** (a) Temperature dependence of reduced Young's modulus $\Delta Y/Y_{97\,K} = (Y - Y_{97\,K})/Y_{97\,K}$ in the heating process in annealed γ-$Na_{0.66}CoO_2$ (square) and as-prepared γ-$Na_{0.66}CoO_2$ (circle). The equation of the fitting line is $\Delta Y/Y_{97\,K} = 0.03287 - 0.00033 \cdot T$. (b) Fitting of the internal friction peak in as-prepared γ-$Na_{0.66}CoO_2$ sample (line, Eq. (4) in the text, circle, experiment data in the heating process).

$Q_M^{-1}$ is a constant, $T_M$ the peak temperature, $\tau$ the relaxation time, and $k_B$ the Boltzmann constant. The background internal friction below 220 K is supposed to be a linear function with temperature

$$Q_B^{-1} = Q_0^{-1} + \alpha \cdot T \quad (3)$$

Then the overall internal friction is fitted by the following function

$$Q^{-1} = Q_B^{-1} + Q_D^{-1} \quad (4)$$

The satisfactory fit results are the activation energy $E = 0.22$ eV and preexponential frequency factor $\tau_0 = 2.7 \times 10^{-9}$ s, which is shown in Fig. 4b. This preexponential frequency factor is larger than the typical value, which is an order of $10^{-12}$ s.

Since above form of background internal friction in as-prepared γ-$Na_{0.66}CoO_2$ is chosen arbitrarily, another fitting procedure is taken. As we found, the internal friction below 240 K in annealed γ-$Na_{0.66}CoO_2$ sample can be fitted by (the data not shown here)

$$Q_A^{-1} = Q_1^{-1} + Q_2^{-1} \cdot \exp\left(-\frac{\Delta}{T}\right) = 0.00025 + 0.072 \cdot \exp\left(-\frac{732}{T}\right) \quad (5)$$

This temperature dependent internal friction is ascribed to the freezing process below 240 K. Since similar freezing process is observed in as-prepared γ-$Na_{0.66}CoO_2$, the overall internal friction in as-prepared sample could be fitted by

$$Q^{-1} = Q_A^{-1} + Q_D^{-1} = Q_1^{-1} + Q_2^{-1} \cdot \exp\left(-\frac{732}{T}\right) + Q_D^{-1} = 0.00092 + 0.029 \cdot \exp\left(-\frac{732}{T}\right) + \frac{0.00061 \times 163}{T} \cdot \mathrm{sec}\,\mathrm{h}\left(1337 \cdot \left(\frac{1}{T} - \frac{1}{163}\right)\right) \quad (6)$$

where $\Delta = 732\,\mathrm{K} \approx 95$ meV is fixed in advance (data not shown here). The satisfactory fit results are the activation energy $E = 0.17$ eV and preexponential frequency factor $\tau_0 = 2.6 \times 10^{-8}$ s.

This preexponential frequency factor is much larger than the typical value. The failure of the fitting might be due to the assumption of a single-time Debye relaxation. This suggests that the relaxation process is characterized by a spectrum of relaxation times.

Using Eq. (2) and following equation:

$$\omega \cdot \tau(T_M) = 2\pi f \cdot \tau_0 \cdot \exp\left(\frac{E}{k_B T_M}\right) = 1 \quad (7)$$

another activation energy 0.38 eV is obtained where the preexponential frequency factor and peak temperature is set in advance, $\tau_0 = 1 \times 10^{-12}$ s and $T_M = 163$ K. However, the activation energy 0.22 eV or 0.38 eV is smaller than the typical value, 0.6 eV for isolated oxygen vacancies and 1.0 eV for aggregated vacancies in $SrTiO_3$ [33]. Then it is supposed that the anelastic relaxation is some kind of strain induced off-center hopping of the atoms nearby the oxygen vacancy. In fact, the off-center configuration of sodium is proposed in oxygen stoichiometric $Na_{0.74}CoO_2$ and $Na_{0.38}CoO_2$ [32]. Then the internal friction peak in as-prepared γ-$Na_{0.66}CoO_2$ is expected for sodium off-center hopping near oxygen vacancies. The atomic off-center hopping anelastic relaxation has been used to interpret the internal friction peaks in $YBa_2Cu_3O_{7-\delta}$ with the activation energy 0.16 and 0.19 eV [34,35].

## 4. Summary

A transition behavior of internal friction was observed in $Na_{0.66}CoO_2$ around 240 K, which is proposed to be the freezing transition of the mobility of sodium atoms. A superposed internal friction peak around 160 K was observed in as-prepared sample, which is absent in annealed one. This peak is suggested to be atomic off-center hopping near oxygen vacancies.

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