Identification of Cobalt Oxides with Raman Scattering and Fourier Transform Infrared Spectroscopy

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ABSTRACT: Although Raman spectral fingerprints of Co3O4 have been well established, the infrared spectrum of Co3O4 is less understood due to its dependence on sample morphologies and experimental configurations. The same is true for both Raman and infrared spectra of CoO. In this study, we present a comprehensive optical characterization of Co3O4 and CoO with Raman scattering and Fourier transform infrared spectroscopy (FTIR). Two of the transverse optical (TO) phonons and their corresponding longitudinal optical (LO) phonons of Co3O4 above 500 cm−1 are observed in both transmission and diffuse reflectance with LO/TO intensity ratios depending on particle size and the incident angle of FTIR beam. CoO is featured by a broad infrared band around 510 cm−1. In contrast to many previous reports, no Raman-active phonon line is observed, which is in agreement with the selection rule for rock-salt CoO. Nevertheless, CoO can still be characterized by Raman scattering from magnetic excitations in its antiferromagnetic phase at low temperature and a two-phonon Raman band at ∼1060 cm−1.

1. INTRODUCTION

As the only two stable oxides of cobalt, Co3O4 and CoO have attracted increasing attention due to their remarkable magnetic, optical, electronic, and chemical properties. They have found a wide range of applications in catalysis, lithium-ion battery, solar energy, spintronics, and gas sensing.1−10 Nanostructures of cobalt oxides with different morphologies and sizes have been synthesized for better performances or new applications. Raman scattering and Fourier transform infrared spectroscopy (FTIR) are powerful and noninvasive characterization techniques used to identify and characterize cobalt oxides but many of reported spectra do not agree with each other. For example, Tang et al. observed two broad Raman bands at 455 and 675 cm−1 in CoO nanoparticles,11 but Wang and Zhang showed two bands at 477 and 671 cm−1 in CoO nanowires.12 Gallant et al. observed higher frequency bands and assigned them to A1g and Eg modes of CoO.13 Very different sets of three Raman bands were reported by several groups14−16 and were further assigned to A1g, Eg, and T2g modes by Ravindra et al.16 Four Raman bands were also reported by Choi et al. in CoO powders and CoO electrode.17 In contrast, earlier work by Struzhkin et al. showed that CoO does not have any phonon Raman bands in the similar range but has a two-phonon Raman peak at 697 cm−1.18

For FTIR of CoO, it was understood that the spectrum is characterized by a transverse optical (TO) phonon below 400 cm−1 and a higher frequency longitudinal optical (LO) phonon but different values of LO has been reported by many groups. Tang et al. reported a broad absorption band at 507 cm−1 from transmission of CoO powder sample;11 Barakat et al. observed a similar absorption band below 500 cm−1 in CoO nanofibers.19 Using reflectance and subsequent modeling of dielectric function of single crystal, Kant et al. obtained a LO of 562.1 cm−1.20 Higher-frequency bands in the range of 577 and 598 cm−1 were also reported by Lenglet et al. and Pfeil et al.21,22 For Co3O4, the “standard” Raman spectrum was already established by one of the authors.23 Infrared spectrum of Co3O4 was also investigated by Shirai et al., who obtained all IR-active phonon modes from reflection spectra in combination with Kramers–Kronig transformation and oscillator fit.24 Absorption-like spectra of both TO and LO phonons were reported by Lenglet et al., who measured reflectance spectrum of oxidized Co plate.24 Their approach was simple except that oxidized cobalt contained mixed Co3O4 and CoO phases, and the phonon frequencies depended on the thickness of oxidized film and angle of incident IR beam.21 Despite these earlier works, only two instead of four absorption bands above 500 cm−1 were observed and used as the IR signature of Co3O4 by many groups with frequency varying from one group to another.11,22,25−33

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These apparent discrepancies and lack of well-established spectra make it difficult to accurately identify cobalt oxides and understand their basic properties and will hinder their potential device applications. Using highly pure cobalt oxide thin films and powders, we first show the observation of all four LO/TO bands in both transmission and diffuse reflectance modes and then we explain how the experimental configuration and particle size will affect the relative intensity of LO versus TO. Having established the infrared spectrum of Co$_3$O$_4$, we identify the LO of CoO by correlating IR spectrum with oxidation state of Co between CoO and Co$_3$O$_4$. Using laser-induced oxidation, we disprove the 697 cm$^{-1}$ line as a two-phonon Raman but confirm the broad 1060 cm$^{-1}$ band as a two-phonon Raman by the observation of a small spectral shift with different laser lines. Such a complete set of Raman and FTIR spectra will provide a guideline for the future identification of cobalt oxides.

2. SAMPLE PREPARATION AND CHARACTERIZATION

Cobalt oxide thin films and powders were prepared for Raman and FTIR study because they are the most common forms of nanomaterials. One hundred nanometers thick Co$_3$O$_4$ films for FTIR were deposited on double side polished silicon wafers using an AJA ATC 2200 ultrahigh vacuum DC magnetron sputtering system with argon and oxygen flow rates of 35 and 5 sccm, respectively. High purity Co$_3$O$_4$ powders were purchased from Sigma-Aldrich with average sizes of 10 μm and 50 nm. Particles with less than 50 nm (10–50 nm) were obtained by ball milling 10 μm Co$_3$O$_4$ powders for 16 h in a SPEX Mixer/Mill (SamplePrep 8000M). Co$_3$O$_4$ powders were converted from CoO by ball milling 10 μm Co$_3$O$_4$ powders via thermal decomposition. In some cases, such-obtained CoO powders were further annealed in H$_2$ environment at 200 °C for 2 h to remove residue Co$_3$O$_4$. The transformation from CoO to Co$_3$O$_4$ powders was achieved by annealing CoO powders on a hot plate in air at various temperatures up to 800 °C. A Co foil was also heated in air at 800 °C to form a surface Co$_3$O$_4$ layer and was then thermally decomposed to become CoO thin film.

FTIR was performed using a Thermo Nicolet iS50 spectrometer equipped with a DTGS detector at room temperature in the range of 4000–400 cm$^{-1}$. To perform diffuse reflective FTIR (DRFTIR) measurement, KCl was mixed with cobalt oxide powders. Raman measurements were performed using a Horiba Triax550 and a T64000 spectrometers in a backscattering configuration.

3. RESULTS AND DISCUSSION

3.1. LO and TO Spectra of Co$_3$O$_4$ Film by FTIR Transmission. Infrared absorption through transmission measurement is the most straightforward experimental configuration of FTIR for thin film samples. However, conventional transmission with IR incidence normal to the film can only probe TO; previous observations of both LO and TO bands were achieved in reflection mode. An easy method to avoid this drawback of conventional transmission is to rotate the sample so that incident beam has a large angle from the normal of the film. As shown in Figure 1a,b, only in oblique incidence the electrical field of infrared beam is able to couple to the polarization of LO phonons. As expected, the spectrum in Figure 1c is dominated by two TO modes with normal incidence but when the incident angle increases, the corresponding LO modes begin to appear and become stronger. Note that the incident beam is not polarized, only p-polarized light is coupled to LO and s-polarized beam is not coupled to LO at any angles; this is why two TO bands are still stronger than LOs even at an angle of 80°. Another important observation is that the positions of all four phonons stay the same even when the angle varies.

3.2. LO and TO Spectra of Co$_3$O$_4$ Powders by Diffuse Reflectance FTIR. Transmission and reflection are good for thin films and thick single crystal samples with smooth surfaces, but for powder samples diffuse reflectance FTIR (DRFTIR) is a more convenient and effective method. Furthermore, DRFTIR allows people to obtain absorption spectrum through the Kubelka-Munk (KM) function $KM(R) = (1 - R)^2/2R \sim \alpha$, where $R$ is diffuse reflectance and $\alpha$ is absorption coefficient. Figure 2 shows DRFTIR spectra of Co$_3$O$_4$ with three different particle sizes. Like transmission with a large incident angle above, all four phonons can be observed, but LO phonons appear stronger than TO modes, and the LO/TO intensity ratio increases when the average particle size decreases. Again, no noticeable change in the phonon peak position and line width is observed. The reason for the appearance of LO modes in diffuse reflectance spectra is that DRFTIR involves multiple reflections and transmissions through the Co$_3$O$_4$ particles at...
mostly oblique angles facilitated also by the KCl filler. As the particle size in the powder decreases, the normal reflecting particle surface diminishes as well due to the increase surface curvature. This, along with the increased scattering at large angles, results in the enhanced LO to TO intensity ratio.

3.3. LO Spectrum of CoO by Diffuse Reflectance.

DRFTIR was also employed to measure the LO spectrum of CoO powders. The TO phonon of CoO cannot be accessed by our system due to the limit of beam splitter and detector. Figure 3a shows the spectra of CoO obtained from 10 μm Co3O4 powders and similar spectra were also observed in CoO decomposed from 50 nm Co3O4 nanoparticles. On the basis of DRFTIR of Co3O4 and a previous study, the broad peak centered at 510 cm\(^{-1}\) is assigned to the LO of CoO, which is very close to the spectrum reported by Tang et al.\(^\text{11}\) A weak peak of Co3O4 phonon at \(\sim 656\) cm\(^{-1}\) can also be seen in Figure 3a in CoO without H\(_2\) treatment. Figure 3b shows the corresponding XRD spectra; no Co3O4 can be observed, indicating that DRFTIR is a more sensitive technique than XRD. A side effect of annealing in H\(_2\) is that a small amount of metallic Co was also produced, as revealed by XRD.


To further confirm the phonon spectrum of CoO and its relationship with that of Co3O4, we gradually oxidized CoO powders by heating in air on a hot plate and monitored the evolution of the spectrum. Figure 4a shows the DRFTIR spectrum after CoO was heat treated for 2 h at 300, 500, and 800 °C. It is well-known that CoO will transform to Co3O4 when oxidized in air. This transformation can be clearly seen; phonons of Co3O4 grow and the broad absorption feature of CoO begins to decrease when the temperature increases. This structural transition is also captured by XRD in Figure 4b, except that no Co3O4 was detected at 300 °C although two TO bands of Co3O4 are very visible, which further confirms that DRFTIR is a more sensitive technique than XRD. An interesting observation is that unlike DRFTIR of Co3O4 powders, TO is much stronger than LO at the early oxidation stages. This is because Co3O4 starts from a thin shell on CoO core due to the oxidation CoO particles in air. For a thin shell or film, TO is the dominant feature of the spectrum, similar to the transmission spectra shown in Figure 1.

The FTIR spectra can also be used to monitor the reverse process, that is, the decomposition of Co3O4 to CoO, during which oxygen will be released. Figure 5a shows the change in O\(_2\) concentration when 10 μm Co3O4 powders were annealed in an Ar atmosphere (225 sccm) from 350 to 950 °C at a heating rate of 20 °C per minute. It can be seen that the decomposition started at \(\sim 700\) °C and ended at \(\sim 870\) °C, similar to previous observations.\(^\text{11}\) On the basis of the oxygen release information, we annealed the Co3O4 powders at 700 °C for 60 min, 850 °C for 90 min, and 950 °C for 180 min; the annealed samples were denoted as Co-700, Co-850, and Co-950, respectively. The corresponding XRD patterns and FTIR spectra in Figure 5b,c confirm the transition from Co3O4 to CoO. Unlike the oxidation of CoO, the thermal decomposition...
of Co\textsubscript{3}O\textsubscript{4} requires a higher temperature, indicating that Co\textsubscript{3}O\textsubscript{4} is more stable in air than CoO.

3.5. Raman Spectrum of CoO. In defect-free CoO single crystals, the first-order phonon Raman scattering is forbidden according to the selection rules for the NaCl-type centrosymmetric lattice structure. In fact, as discussed above, CoO has three branches of optic phonons: two degenerate TO modes and one LO mode.\textsuperscript{36} They are infrared active and cannot be Raman active in crystal lattice with center inversion symmetry. The second-order two-phonon Raman scattering, however, is allowed, and accounting for the phonon dispersion of CoO,\textsuperscript{36,37} it should appear in the 1000–1100 cm\textsuperscript{-1} spectral range. Figure 6 shows the Raman spectra of H\textsubscript{2} annealed CoO film on Co foil measured in vacuum and at three different temperatures with the 514 nm laser excitation at very low power. The room-temperature Raman spectrum of CoO is essentially the same as the bottom spectrum in Figure 6. The Raman spectra of pure CoO above 200 K, in which CoO is in paramagnetic state, are dominated by a broad band at \textasciitilde1060 cm\textsuperscript{-1}, which is consistent with the expected second-order Raman scattering from optical modes in CoO.\textsuperscript{36} Similar band has also been reported by Struzhkin et al.\textsuperscript{38} In addition, a weak band at 500–550 cm\textsuperscript{-1} is seen with varying spot-to-spot intensity. On the basis of the results of the lattice dynamics calculations,\textsuperscript{36,37} we assign this band to the defect-induced one-phonon density of states scattering in CoO. With decreasing temperature below 200 K, three new sharp peaks start to grow. They represent the Raman scattering from magnons in the antiferromagnetic CoO.\textsuperscript{38,39} At this point, we suggest that the ultimate Raman test for confirming the presence of CoO in a cobalt oxide mixture is the measurement of the magnon lines at low temperatures.

In the same study, Struzhkin et al. also observed a sharp peak at 697 cm\textsuperscript{-1} and assigned it to two-phonon Raman of CoO.\textsuperscript{38} To investigate the origin of this line, we performed measurement at room temperature in another pure CoO sample. Figure 7 shows the Raman spectrum of CoO before and after the illumination of larger laser power (70 mW) for 2 min. This sharp line was observed only after laser heating, indicating that this line originates from CoO\textsubscript{4} due to partial oxidization of CoO by local laser heating. Figure 7a also shows the difference in Raman with two laser lines. A spectral shift of Raman band can be observed when the excitation energy is changed, a characteristic of two-phonon Raman.

3.6. More Discussion. We believe the reason why only two peaks were observed in previous FTIR studies of CoO\textsubscript{4} is because transmission with normal incidence was used.\textsuperscript{11,22,25–33} The reported high-frequency TO band of CoO\textsubscript{4} has a similar frequency as what we have observed around 660 cm\textsuperscript{-1} but the low-frequency TO band is 15–30 cm\textsuperscript{-1} higher than our observation of \textasciitilde555 cm\textsuperscript{-1}.\textsuperscript{11,22,25–33} On the basis of our
consistent observation of this TO in thin films and powders, as well as previous studies by Shirai et al. and Lenglet et al., we believe that ~555 cm\(^{-1}\) is a more accurate value of CoO TO. For Raman of CoO, many observed lines in the range of 450–700 cm\(^{-1}\) could come from partially oxidized CoO, or structural defects and impurities of CoO. Our observed CoO LO frequency of 510 cm\(^{-1}\) is at least 50 cm\(^{-1}\) lower than those obtained from reflectance measurement of single crystals or thin films, but this value agrees well with ab initio calculation\(^{36}\) and two-phonon Raman of CoO agree well with theoretical calculation\(^{36}\) and two-phonon Raman of CoO, or partially oxidized CoO, or structural defects and impurities of CoO.

In summary, we have demonstrated that all four phonons above 300 cm\(^{-1}\) can be identified from Raman scattering of CoO, or partially oxidized CoO, or structural defects and impurities of CoO.

4. CONCLUSIONS

In summary, we have demonstrated that all four phonons above 500 cm\(^{-1}\) can be observed in thin films and powders of CoO. Under certain conditions, two-phonon Raman scattering of CoO agree well with theoretical calculations. For thin films, a large oblique incident angle is required to observe both TO and LO phonons, but for particle or powder samples diffuse reflectance is a convenient, effective, and safe method. Intensity of laser excitation should be kept low in CoO Raman scattering in order to avoid thermal oxidation of CoO. Our optical spectroscopic techniques and self-consistent spectra will accelerate the progress in basic understanding and future applications of cobalt oxides.

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