

Structural changes of Na_xCoO_2 ($x = 0.74$) at high pressures

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Abstract

Structural changes in the layered compound $\gamma\text{-Na}_x\text{CoO}_2$ ($x = 0.74$) are studied by in situ Raman scattering and energy-dispersive X-ray diffraction methods at pressures up to 41 GPa. The pressure dependence of the lattice parameters indicate that $\gamma\text{-Na}_x\text{CoO}_2$ has a strong anisotropic compressibility before 15 GPa and the unit cell is easily compressed between layers. The discontinuity of the lattice parameters and Raman observations reveal that a phase transition occurred at pressures between 10 and 12 GPa. The high-pressure phase has the same hexagonal symmetry and the phase transition may be due to the pressure-induced rearrangement of one of the Na cations in the unit cell.

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1. Introduction

The layered alkali metal (A) oxides of cobalt, A_xCoO_2 with a triangular Co sublattice and a layer sequence of $\text{A}_x\text{-O-Co-O}$ have been studied since 1970s [1]. They have received considerable attentions recently [2–6] not only in the physical aspect of the two-dimensional (2D) nature, but also in their potentials for practical applications, such as Li_xCoO_2 has already been used as a cathode material [7] in commercialized lithium-ion rechargeable batteries. The recent interest in the Na counterpart is particularly due to its potential for thermoelectrics [8] and the discovery of the superconducting phase [9] of hydrated $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$.

In general, A_xCoO_2 consists of hexagonal layers of A^+ ions sandwiched between edge-shared CoO_6 octahedral layers and the Van der Waals corridors between the neighboring CoO_2 layers are wide enough for the A^+ cations to move, which is the origin of ionic conductivity

for these materials. Previous experimental results [1–10] indicate that both the structural and electronic state of Na_xCoO_2 is very rich with the change of the Na content x . There are at least five phases of Na_xCoO_2 with different Na content x . The structure of Na_xCoO_2 with $x \sim 0.75$, which is called the γ phase, have a hexagonal unit cell [1,6] with space group of $P6_3/mmc$ and lattice constants of $a = 2.84 \text{ \AA}$ and $c = 10.811 \text{ \AA}$ at room temperature (Fig. 1a). However, recent neutron diffraction experiments [11] reveal that there are two different structures for this phase. They both have the same lattice parameters and space group only with a slight difference in the second Na position in the unit cell. The previous structure data shows that the second Na ion occupies the $2d$ position in the γ phase, while the neutron diffraction results suggest the existence of another phase (γ' -phase), where the second Na ion occupies the Wyckoff position of $6h$. The γ to γ' phase transition can not be identified by X-ray diffraction techniques due to the very close structures, but it can be detected by scanning calorimetry, magnetization and transport measurements [11,12]. In fact, the $6h$ site is a split position in the space group of $P6_3/mmc$ and Fig. 1b

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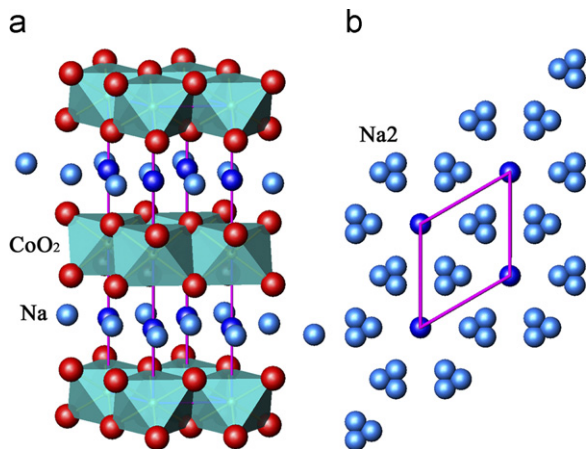


Fig. 1. Schematic diagram of crystal structure of Na_xCoO_2 : (a) γ -phase and (b) Na layers in γ' -phase. The Na atoms are not fully occupied and the Na2 atoms in the γ' -phase ($6h$) are split into 3 positions.

shows the Na layers in the γ' -phase of Na_xCoO_2 . The only difference is that site $2d$ (occupied by Na2) in the γ -phase has been split into three sites ($6h$) in the a - b plane of the γ' -phase. The Na atoms are not fully occupied in both of γ and γ' -phase. Na2 has half occupancy and Na1 has only one quarter occupancy in the $2b$ site.

The phase stability and phase transition of Na_xCoO_2 with variation of Na content x and temperature has been widely investigated before [1,10,12]. Besides the composition and temperature, the third important parameter is pressure and many pressure-induced structural changes have been observed in oxides [13,14] and other materials [15]. However, no work about pressure effect on the structure of Na_xCoO_2 is reported as far as we know and there are only a few reports [16,17] about the pressure effect on the superconducting hydrate $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ in a quite low pressure region. We present here from a systematic study on the structural change of the γ - Na_xCoO_2 at high pressures by using in situ Raman scattering and X-ray diffraction methods.

2. Experimental methods

The Na_xCoO_2 sample was synthesized by solid state reaction method. Well-mixed powders of $0.9/2\text{Na}_2\text{CO}_3 + 1/3\text{Co}_3\text{O}_4$ were pressed into pellets and heated at 850°C for 12 h in air, then reshaped and heated at 950°C for another 12 h. The sodium has lost some content due to the evaporation during heating. The powder X-ray diffraction measurements confirmed the single hexagonal phase for the final product. Pressure was generated with diamond anvil cell (DAC) techniques by pressing a pair of diamond anvils with culet size of 0.35 mm. Stainless steel gaskets were used for both XRD and Raman measurements. Raman spectra were collected by using a high throughput holographic imaging spectrograph with volume transmission grating, holographic notch filter and a thermoelectrically cooled CCD detector (Physics Spectra). The light is from a He–Ne

laser with wavelength of 783.54 nm and the laser power is controlled below 5 mW to avoid heating the sample. The in situ high-pressure XRD measurements were performed with synchrotron radiation X-ray source at station B1, Cornell High Energy Synchrotron Source (CHESS) in energy-dispersive mode. The diffraction patterns are collected with a multi channel detector, which is fixed at 2θ angle of 15° . The energy is calibrated with well-known radiation sources (^{55}Fe and ^{133}Ba) and the 2θ is calibrated with the Bragg peaks from standard gold powder. The XRD peaks are fitted individually and the unit cell is indexed by least square method with program Unitcell [18]. A standard methanol/ethanol (4:1) pressure medium is used for all the experiments and this pressure medium can, in general, keep the hydrostatic condition at pressures below 10 GPa. The pressure in all the experiments was measured by the ruby fluorescence method [19].

3. Results and discussions

The structure of the synthesized sample is checked with a lab X-ray diffraction facility and the XRD pattern verifies the single phase of γ - Na_xCoO_2 . Due to the evaporation of Na, the real value of its content x is smaller than that in the starting material. Rietveld refinement with the structural model in the literature leads to x of 0.74 for our sample and lattice parameters of $a = 2.8416(3)\text{\AA}$ and $c = 10.922(2)\text{\AA}$, which is in good agreement with those reported before [1].

Raman scattering is a very powerful method in detecting the local structural changes of atoms in the unit cell. There are several reports [20–23] up to now on the Raman measurements for the nonhydrated and hydrated Na_xCoO_2 with different Na content. The reported Raman active modes and their positions are not well in agreement from one another. This may be due to the different sample source and the sodium content in the sample. In fact, Na_xCoO_2 is air sensitive, and long time keeping in air will result in structural changes. We have measured the Raman spectrum for fresh Na_xCoO_2 sample at different pressures and the spectra are shown in Fig. 2. The sample is in dark blue color and the Raman spectrum is quite weak in intensity, but several Raman active modes are clearly observed in the whole measured pressure range. The position of the observed modes at room conditions is compatible with those observed in the polycrystalline samples [21] except with an additional mode centered at 194cm^{-1} . However, this is the E_{1g} mode for Na_xCoO_2 , which was observed in single crystal samples [22]. A symmetry analysis taking into account the $P6_3/mmc$ space group for γ - Na_xCoO_2 gives the following Raman-active modes:

$$\Gamma = A_{1g} + E_{1g} + 3E_{2g}.$$

There are four modes observed in our sample at low pressures and their positions are 195, 471, 582 and 698cm^{-1} , respectively, at 1.3 GPa. According to theoretical calculations and polarized Raman measurement from

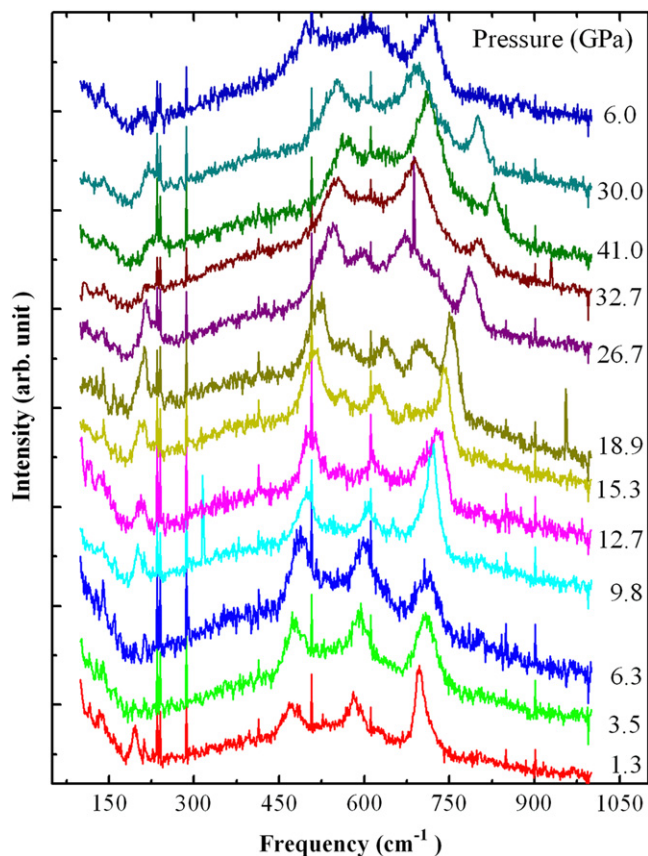


Fig. 2. Raman spectrum of Na_xCoO_2 measured at different pressures. A pressure-induced phase transition occurred at 10 GPa.

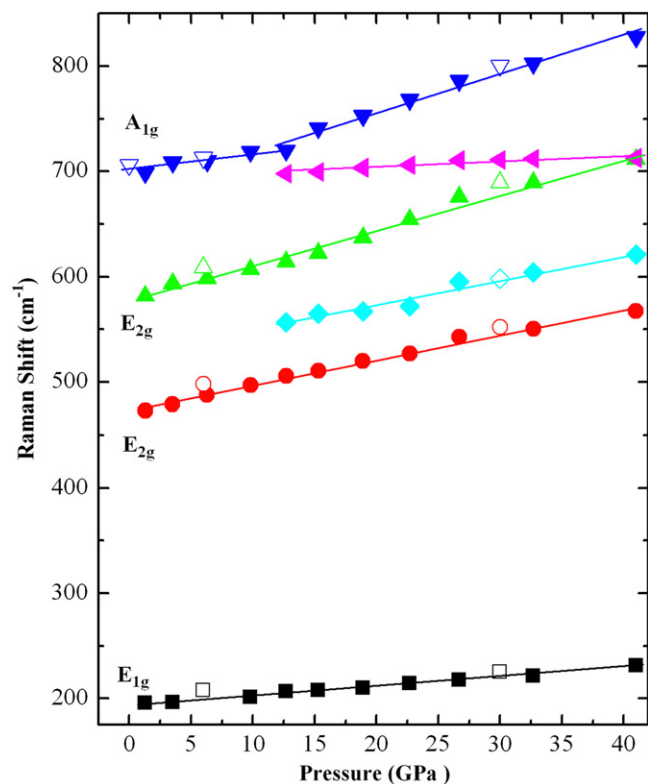


Fig. 3. Pressure dependence of the frequency of the observed Raman modes for the hexagonal Na_xCoO_2 . The open symbols correspond to the data measured during release of pressure.

single crystals [21,24], the strongest mode at 698 cm^{-1} is the A_{1g} mode and the 195 cm^{-1} is the E_{1g} mode. These four modes are clearly observed in our sample till to 10 GPa. After that, the A_{1g} mode began to split into a sharp peak and a broad one, and a new weak mode between the two E_{2g} modes appeared. With further increase of pressure, the two split peaks from the A_{1g} mode have different pressure dependence. The broad one has slow pressure dependence and becomes closely to the E_{2g} mode with increase of pressure and they are merged into one peak between 27 and 33 GPa. At least five Raman active modes are observable till to 41 GPa. The pressure dependence of the frequency of the observed Raman modes is plotted in Fig. 3. A pressure-induced phase transition took place between 10 and 12 GPa is clearly observed. There are six modes observed at pressure of 19 GPa, so the high pressure phase should not be the original $\gamma\text{-Na}_x\text{CoO}_2$ because only 5 Raman active modes are allowed. However, all the Raman active modes change continuously with pressure and there is no modes disappearing during the process and the high-pressure phase should have a close structural relation with the $\gamma\text{-Na}_x\text{CoO}_2$. During release of pressure, the spectrum continuously changes back to a spectrum similar with the $\gamma\text{-Na}_x\text{CoO}_2$ except the broadening of the peaks. The broadening of the Raman modes may be due to the stress

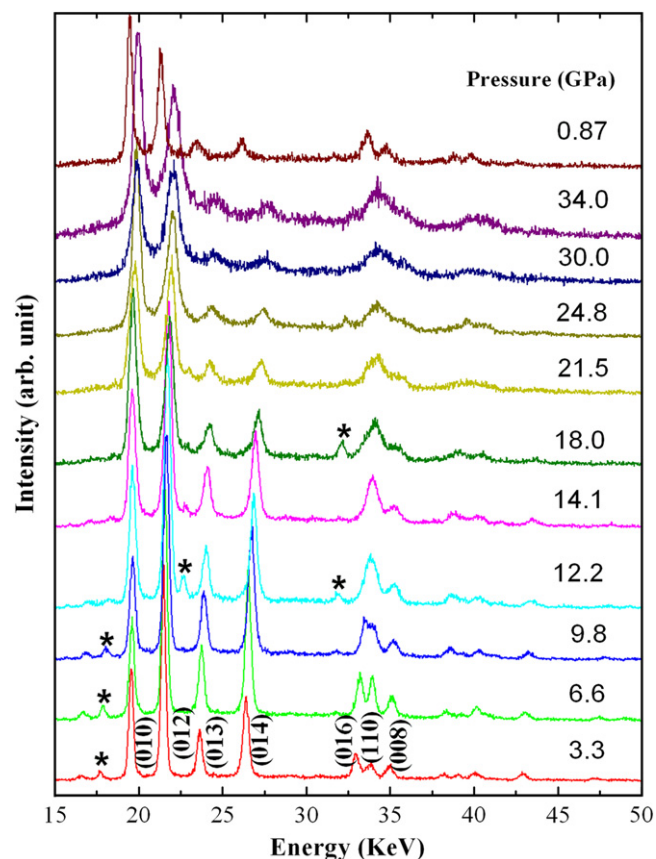


Fig. 4. Energy dispersive X-ray diffraction patterns of Na_xCoO_2 at different pressures. Some weak peaks marked with * are contributed by ruby.

induced by external pressure. The Raman spectra also indicated that the phase transition is reversible.

In order to check the detailed structural changes at high pressures, in situ X-ray diffraction analysis are performed. Fig. 4 is the energy dispersive XRD patterns of γ - Na_xCoO_2 measured at different pressures. Some of the weak peaks marked with * are contributed by ruby. We can see the XRD patterns keep a similar character during the whole process. The first four strong peaks are diffractions from the (010), (012), (013) and (014) planes and the next three weak peaks around 33–35 keV are contributed by the (016), (110) and (008) diffraction planes. With the increase of pressure, the (016) diffraction moves closely to (110) and they merge into one peak before 12.2 GPa. This means that with increase of pressure, the c -parameter of γ - Na_xCoO_2 is easier to be compressed than the other two parameters. This is because atoms between different layers are connected through Van der Waals bonds and they are much weaker compared to the covalent bonds inside the Co–O layers. This phenomenon was also observed in other layered compounds [25,26]. After 12.2 GPa, the combined peaks do not separate any more, which suggests that the c -axis has a similar compressibility with the a -parameter at high pressures. We have indexed all the X-ray diffraction peaks in a hexagonal unit cell and the results are plotted in Fig. 5a. We clearly observed that the c -axis decreases sharply with the increase of pressure below 15 GPa. It is interesting that the a -axis has a discontinuous change at 10 GPa. These results also indicate a possible phase transition at this pressure, which is in agreement with the Raman observations. The calculated unit cell volume in Fig. 5b, however, does not show any discontinuous change with pressure.

The high-pressure phase is also in hexagonal symmetry and XRD is difficult to distinguish the structural details of the high pressure phase from the starting γ - Na_xCoO_2 phase. However, previous reports [11] with neutron diffraction techniques found two different phases in the Na_xCoO_2 with $x = 0.75$. The two phases have a very close structure with the same lattice parameters and space group.

The only difference is the position of the second Na atoms. In the γ - Na_xCoO_2 phase, the second Na occupies the $2d$ position, while it occupies the $6h$ position in the γ' - Na_xCoO_2 (Fig. 1b). This gives us clue that the high-pressure phase may be the γ' - Na_xCoO_2 . The γ' - Na_xCoO_2 phase has 9 Raman active modes: $\Gamma = 2A_{1g} + 2E_{1g} + 5E_{2g}$, due to the split of one of the Na site in the unit cell. The additional new modes observed in Na_xCoO_2 at high pressures may be attributed to the γ' -phase. However, there is no report on the Raman measurements for the γ' -phase till now. The $6h$ position in the γ' -phase is split into three positions in the Na layer. The Na2 atoms should have a larger freedom to move in the Na layers, so it is easy to understand the expansion of the a lattice parameter at high pressures. According to the neutron diffraction results [11], both the a and c lattice parameters for the γ' -phase are little larger than those of the corresponding γ -phase at normal pressure. However, we did not observe obvious discontinuity for the c -axis during the phase transition of Na_xCoO_2 at high pressures. This can be explained by the pressure effect, because the c -axis for both the γ - and γ' -phases are largely compressed at high pressures and their difference may be unobservable at high pressures. Both Raman and XRD results suggest that the pressure-induced phase transition in Na_xCoO_2 may be due to the phase transition from the γ - to γ' -phase.

When the pressure reaches to 10 GPa, the a -parameter is compressed by 1.6% while the c -parameter is shortened by 5.3%. The decrease of the c -parameter is mainly through squeezing the space of Na layers because the covalent bonded Co–O layers are compact and not easy to be compressed. Further compression of the Na layers will result in the rearrangement of Na ions in order to reduce the system energy.

4. Conclusions

The layered γ - Na_xCoO_2 compound is easily to be compressed along the long c -axis. When pressure is

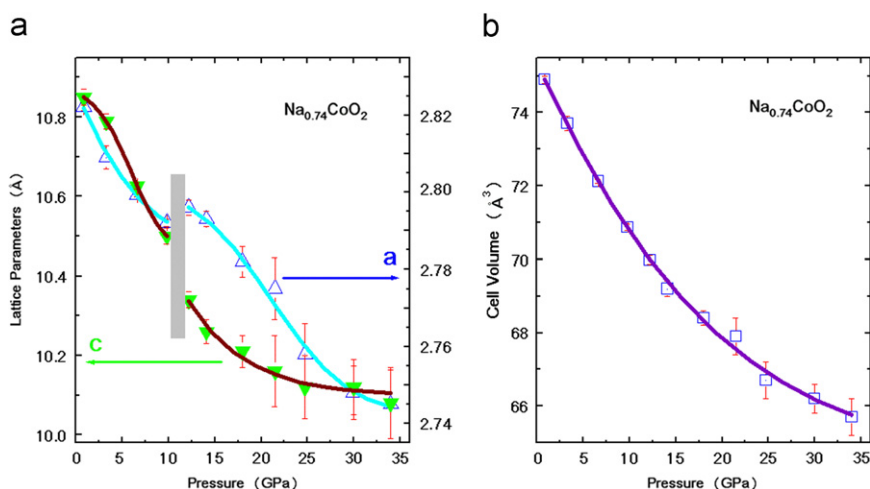


Fig. 5. The structural parameters for the hexagonal Na_xCoO_2 compound at different pressures: (a) lattice parameters; (b) unit cell volume.

increased to more than 10 GPa, a pressure-induced subtle phase transition is observed by using in situ Raman scattering and energy dispersive X-ray diffraction methods. The high-pressure phase is also in hexagonal symmetry and not distinguishable from the γ phase from the X-ray diffraction patterns. The phase transition may be due to formation of the γ' - Na_xCoO_2 at high pressures.

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