Chapter 4

Sample characteristic

4-1 Single crystal

$Na_{0.84}CoO_2$ single crystal was grown by Professor F. C. Chou in the Center for Condensed Matter Sciences of National Taiwan University by using the floating-zone technique. Fig. 4 - 1 shows the X-ray diffraction (XRD) data of this sample. The Na concentration is determined by Electron Probe for Microanalysis (EPMA) results.

4-2 Thin films

Na_xCoO_2 (x = 0.68 and 0.75) thin films were grown by Doctor W. J. Chang in the Department of Electrophysics at National Chiao Tung University. The reactive solid-phase epitaxy (R-SPE) method[70] was applied in the fabrication process, which is described detailed in reference 71. The crystal structure and sodium concentration of Na_xCoO_2 thin films were carefully examined by X-ray diffraction measurements. The results of θ-2θ and Φ scans are shown in Fig. 4 - 2 and Fig. 4 - 3, respectively.[72] The lattice mismatch between the Na_xCoO_2 films and the sapphire substrate is reduced down to ~ 3% by a 30° in-plane rotation with respect to sapphire-(1000), as being illustrated in the Φ scan results of Fig 4 - 3.[72] Since in Na_xCoO_2 cobaltates there exists an intimate correlation between the crystal structure parameters and Na content in the material, the Na content of the obtained Na_xCoO_2 films can be inferred by comparing the lattice constants with the structure phase diagram.[16] Moreover, the $Na_{0.75}CoO_2$ films instantly react with carbon dioxide and

moisture in the ambient environment resulting in loss of sodium (after one hour). This behavior is reflecting in the XRD results shown in Figs. 4 - 2(c) and (d). It is important to note that the signature of Co_3O_4 emerges after longer time. We can see such evidence in XRD results (Figs. 4 - 2(e) and (f)) of Na_xCoO_2 (x = 0.68 and 0.75) thin films which were exposing in ambient environment for more than one day. The temperature-dependent resistivity $\rho_{ab}(T)$ is shown in Fig. 4 - 4, revealing exactly identical temperature dependent behavior to that obtained from single crystal[2] with similar sodium contents of x = 0.68 and 0.75, respectively, indicating the consistency of inferring the film composition by the structural and transport property comparisons.[72] There is another indication of sodium loss, $\rho_{ab}(T)$ (Fig. 4 - 4) where a bended ρ-T curve characterizing $Na_{0.75}CoO_2$ turned into a linear-like curve for $Na_{0.68}CoO_2$ accompanied by a larger residual resistivity after a short period of exposure in air.[72] The in-plane temperature-dependent Seebeck coefficient $S(T)$ is shown in the inset of Fig. 4 - 4.[72] The $S(T)$ curve is similar to that reported by Y. Wang *et al*. in single crystal,[3] revealing another prominent characteristic of this class of materials.

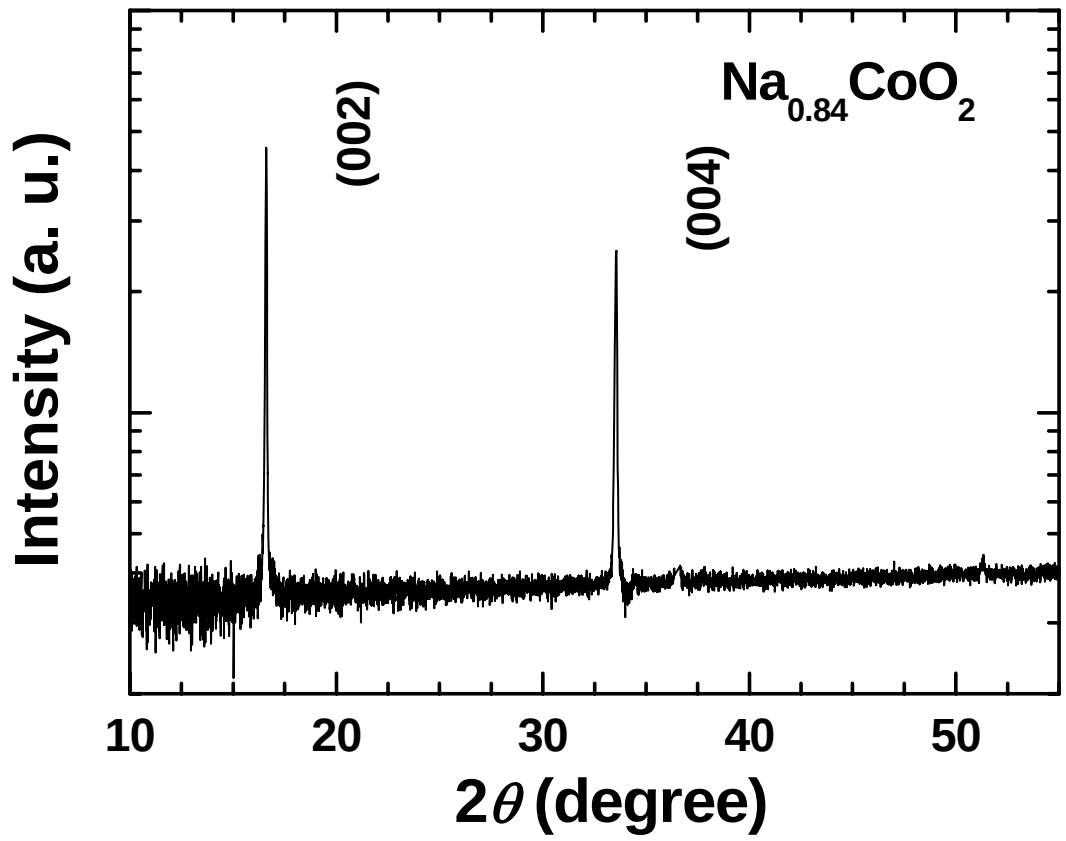

Fig. 4 - 1. The XRD scans of $Na_{0.84}CoO_2$ single crystal.

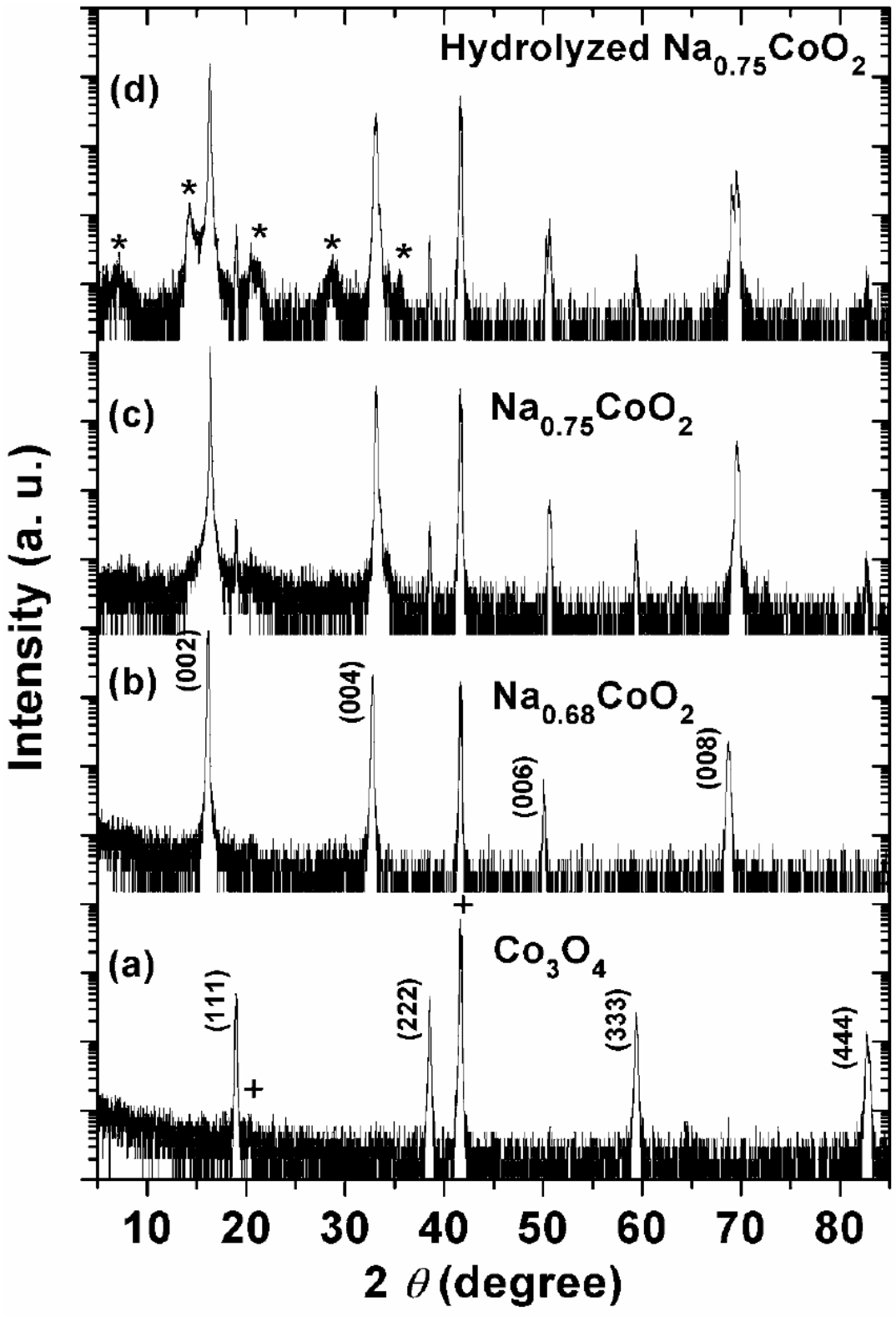

Fig. 4 - 2. The XRD scans of the as-grown samples of (a) Co_3O_4, (b) $Na_{0.68}CoO_2$, and (c) $Na_{0.75}CoO_2$ films. (d) was measured after exposing the $Na_{0.75}CoO_2$ film in the ambient environment at $T = 25$ ℃ and humidity 42 % for 1 hour. The symbols (+) and (*) label the sapphire substrate peaks and hydrolyzed sodium cobalt oxides, respectively.[72]

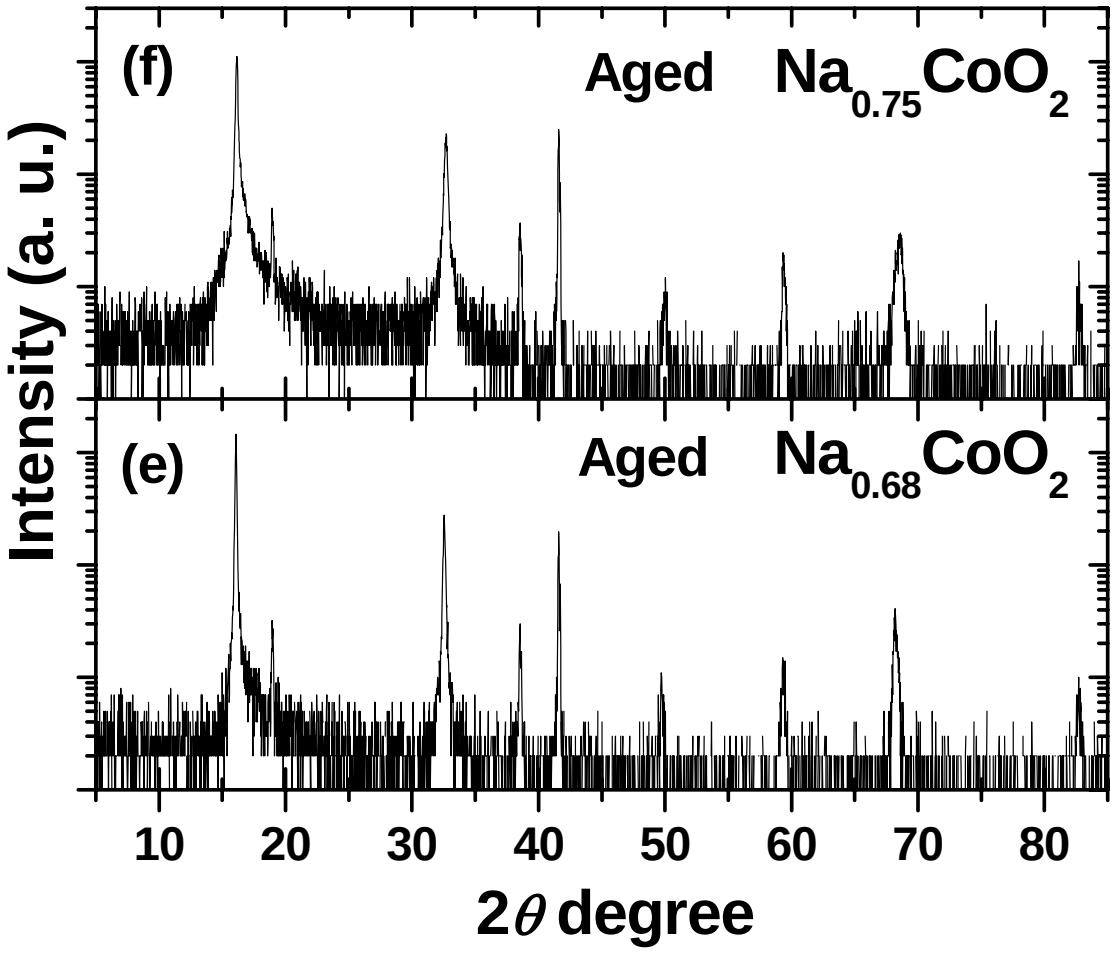

Fig. 4 - 2. The XRD scans of the (e) $Na_{0.68}CoO_2$ and (f) $Na_{0.75}CoO_2$ thin films, which were exposing in ambient environment for more than 1 day.

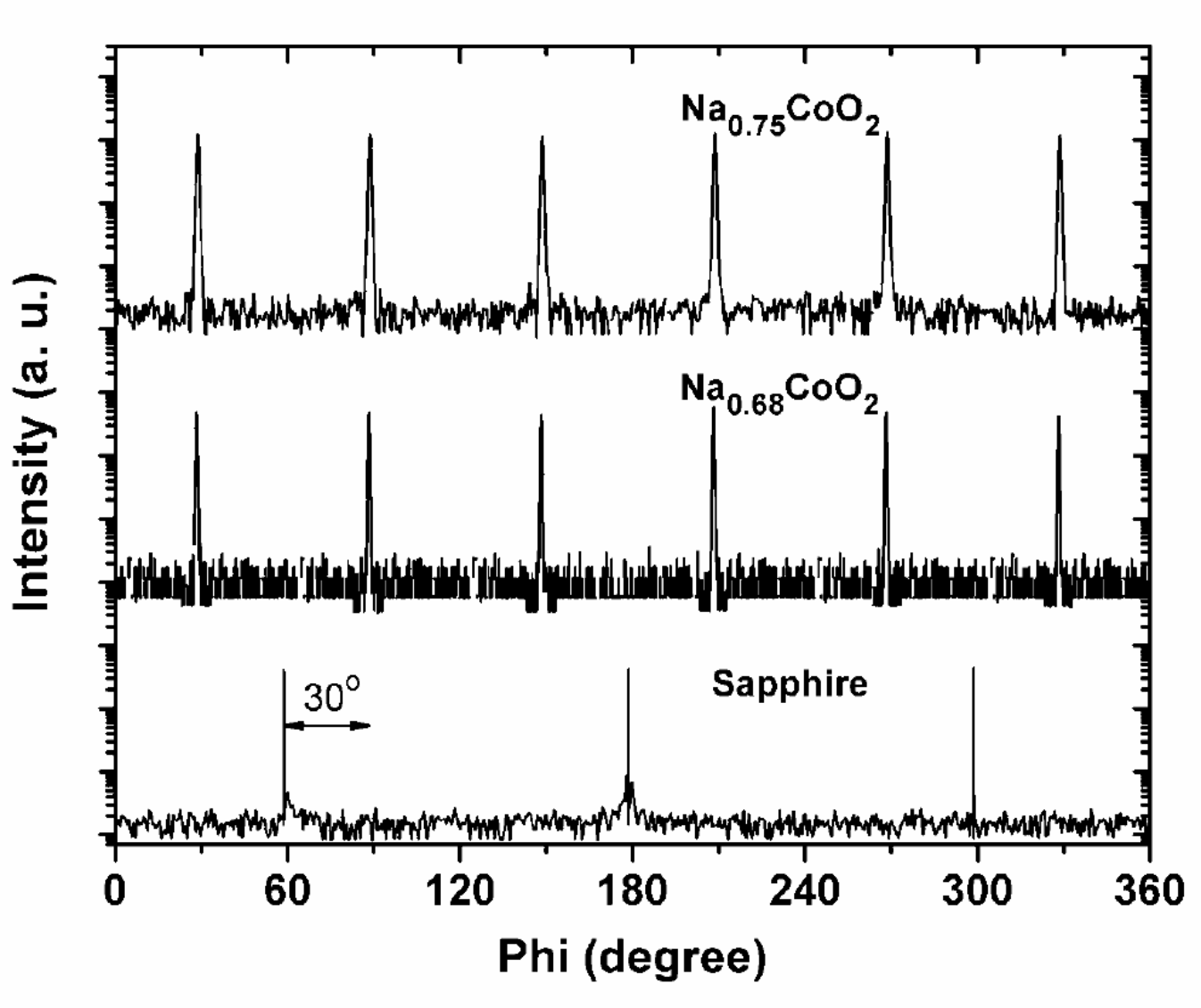

Fig. 4 - 3. *Φ*-scans of the (104) peak of the Na_xCoO_2 films and the sapphire (Al_2O_3) substrate indicate the relative rotation as well as the excellent epitaxial relations between films and substrate.[72]

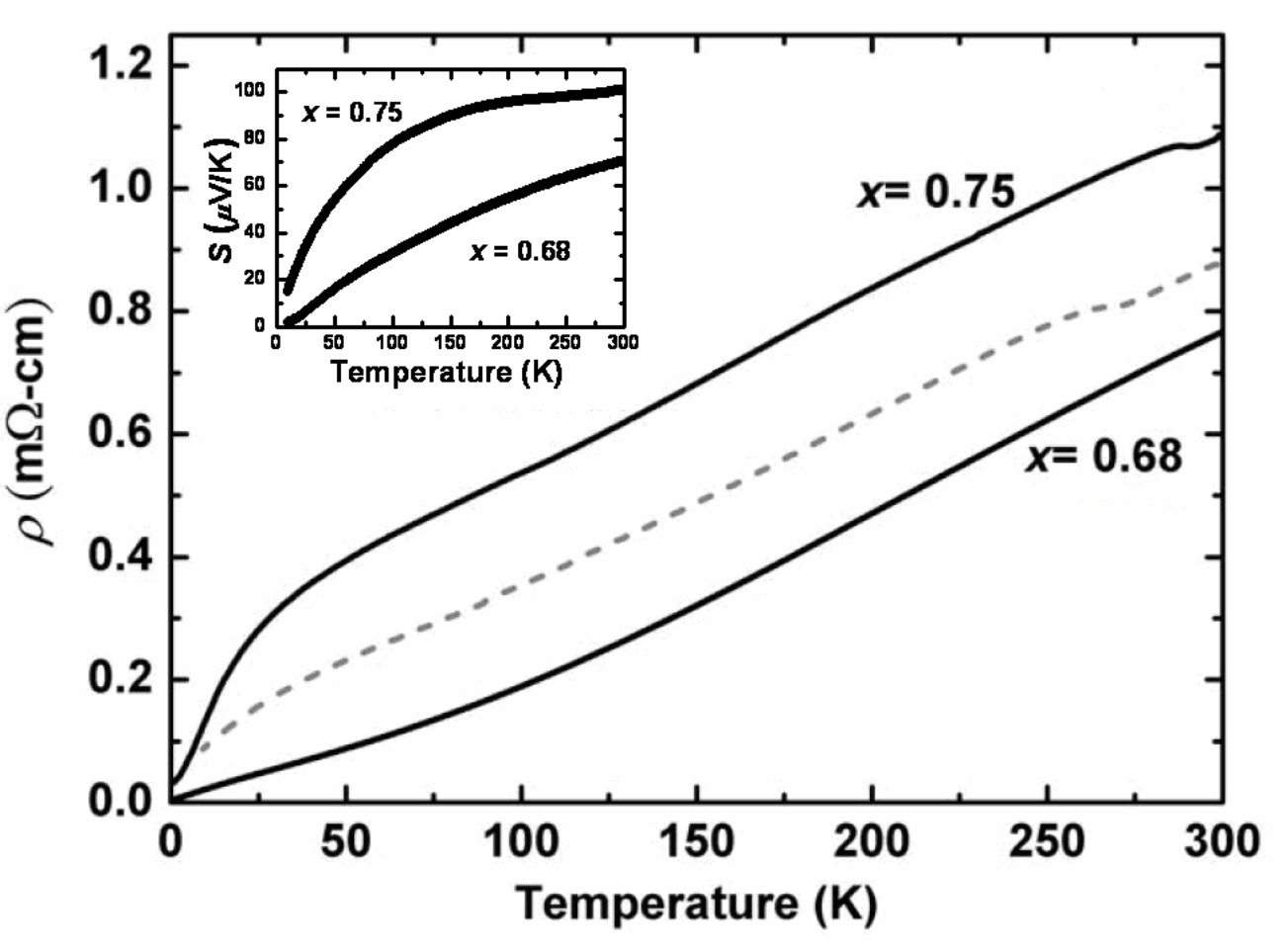

Fig. 4 - 4. In-plane resistivity ρ_{ab} versus T curves (solid lines) of Na_xCoO_2 thin films with x = 0.68 and 0.75. The gray dash line illustrates the ρ_{ab}-T of hydrolyzed $Na_{0.75}CoO_2$ in Fig. 4 - 2(d). Inset: thermopower $S(T)$ measurements for both thin films.[72]