



Low-temperature hydrothermal synthesis of the three-layered sodium cobaltite P3-Na_xCoO₂ ($x \sim 0.60$)



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ABSTRACT

In order to obtain the layered sodium cobalt oxide materials by hydrothermal synthesis, the yield diagram for Na–Co–H₂O system has been built and studied. In the same time, the well-known data of Co–H₂O system have been extended at 250 °C in basic solution.

We had first synthesized directly the high temperature stable phase, P3 – Na_{0.6}CoO₂ by a one-step low-temperature hydrothermal method. The rhombohedral structure of P3 – Na_{0.6}CoO₂ has been determined by X-ray diffraction (XRD) and the purity of phases has been confirmed by XPS. The thermal stability of P3 – Na_{0.6}CoO₂ has been investigated by means of high temperature X-ray diffraction in 298–873 K range and when the temperature has reached 723 K, the completely transformation of P3 – Na_{0.6}CoO₂ in the rhombohedral stable phase α – NaCoO₂ (space group *R-3m*) was observed. Also, a formation mechanism of P3 – Na_{0.6}CoO₂ phase using the unit cell theory in the hydrothermal process was proposed.

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1. Introduction

Layered oxide materials are the new class of materials for thermoelectric applications. In 1997, it was discovered unusually large thermopower and low resistivity in Na_xCoO₂ (NaCo₂O₄) single crystals [1], and found the low thermal conductivity for polycrystalline samples [2]. The crystal structure of Na_xCoO₂ consists in the CdI₂-type hexagonal CoO₂ block and the Na layer which form a layered structure. The Na layer is highly vacant, and the crystal structure changes with the Na content [3,4]. Large thermopower was observed for the $x = 0.5$ – 0.6 sample [1], which is often called γ -phase, Na_xCoO₂ or NaCo₂O₄.

The highly anisotropic of Na_xCoO₂ structure will require strong synthesis efforts, such as texturation techniques, to take advantage of the anisotropic electrical and thermal properties. So far, conventional solid state method was used to prepare the layered sodium cobalt oxides, which involves high temperature, oxygen atmosphere and large time reaction [4]. Previous studies had indicated that in the case of $x = 0.6$ sodium content, only P'3 – Na_{0.6}CoO₂ phase has been obtained by conventional solid-state

reaction route and undergoes a phase transition just above room temperature (350 K) that is associated with an ordering/disordering of the Na⁺ cations in the CoO₂ interslab space, which leads to a high-temperature rhombohedral P3 – Na_{0.62}CoO₂ unit cell (space group *R3m*) [5]. In P3 – Na_xCoO₂ ($x \sim 0.6$), all of the Na⁺ ions occupy a single type of prismatic site sharing a face with a CoO₆ octahedron on one side and edges with surrounding CoO₆ octahedra on the opposite side.

To our knowledge, there have been no reports on yield diagram for Na–Co–H₂O system and pure layered sodium cobalt oxide prepared by hydrothermal method. Continually the revision and improvement of Co–H₂O system is highly stimulated by the numerous uses of cobalt compounds and, in particular, their oxides. Thus, Co–H₂O system was investigated in a temperature range, 25–150 °C, based on revised Pourbaix diagrams, using a new set of standard thermodynamic data in accordance with the recommended CODATA key values [6].

In order to extend the temperature range of interest for hydrothermal synthesis, our work has been firstly focused in the building of the yield diagram for Na–Co–H₂O system at 150–250 °C using XRD results. The yield diagram for Na–Co–H₂O system open the possibility to obtain Na_xCoO₂ phase using soft hydrothermal method. The following stage was to discover the hydrothermal conditions of Na_{0.6}CoO₂ phase synthesis and extra

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oxygen in the hydrothermal solution has been introduced. An unexpected result is that the room temperature rhombohedral P3 – Na_{0.6}CoO₂ phase was obtained by hydrothermal method, contrary a conventional solid-state synthesis which allows only the obtaining a room temperature monoclinic P'3 – Na_{0.6}CoO₂ phase.

2. Experimental

The reagent grade cobalt (II) hydroxide, sodium hydroxide and hydrogen peroxide (30%) were used as starting materials. NaOH is also acts as mineralizer for Co(OH)₂ which has very less solubility. For the building of the yield diagram for Na–Co–H₂O system, the desired Co(OH)₂ quantities were dissolved in NaOH solution. The obtained solution was transferred into Teflon-line autoclave with a volume of 68 ml. The degree of filling the autoclave is 85%. The pressure is less than 50 bar in according with PVT diagram of water [7]. Samples were prepared in the temperature range from 150 °C to 250 °C, reaction time from 24 to 60 h and 1/6 mol/kg of NaOH in an aqueous solution.

In typical synthesis process of layered sodium cobaltite, the desired Co(OH)₂ quantities were dissolved in 4 mol/kg of NaOH in an aqueous solution. After that, the suspension of cobalt (II) hydroxide was oxidized by hydrogen peroxide solution and heating up to 220 °C. In order to respect the pressure safely condition of the Teflon autoclaves, the fill percent of the autoclaves is decreased as hydrogen peroxide concentration is increased. Thus, the fill percent was 30% for 20% hydrogen peroxide concentration. The autoclave was cooled down to room temperature naturally. The precipitate was filtered and washed with deionized water and then, the product was dried at 80 °C.

The structure of products was determined by powder X-ray diffraction (XRD) using Cu-Kα radiation with (λ = 1.5418 Å), in the range 2θ = 10–80°, at room temperature. The data were analyzed by using FULLPROF program [8]. A scanning electron microscope (SEM) was used to observe the size and shape of as synthesized material. X-ray photoelectron spectroscopy (XPS) measurements were recorded using a SPECS XPS spectrometer based on Phoibos 150 electron energy analyzer with non-monochromatic X-rays emitted by an anti-cathode of Mg (1253.6 eV). The analysis chamber was maintained in ultra-high vacuum conditions (~10⁻⁹ mbar). The electron energy analyzer was operated in constant energy mode. Extended spectra, over wide ranges of binding energy (1200 eV), were acquired using an analyzer pass energy of 50 eV. High resolution spectra were collected over smaller ranges (10–30 eV) at 10 eV pass energy giving an energy resolution of 0.7 eV (FWHM of the Ag 3d_{5/2} line). The C(1s) line (at 285 eV) corresponding to the surface adventitious carbon (C–C line bond) has been used as reference binding energy (BE). The recorded XPS spectra were processed using the Spectral Data Processor v 2.3 software. The high temperature behavior of P3 – Na_{0.6}CoO₂ phase has been studied by high temperature X-ray diffraction. The powder sample was placed in an HTK 2000 high temperature chamber. X-ray diffraction data were obtained from 10° to 100° in 2θ with a 0.01 step size over the range up to 600 °C. The heating rate between point was 10 °C/min.

3. Results and discussion

3.1. Yield diagram for Na–Co–H₂O system

The yield diagram for Na–Co–H₂O system with NaOH, 13 mmol/l Co(OH)₂ as precursors was built using XRD patterns. The results are summarized in the Fig. 1.

The study of the yield diagram for Na–Co–H₂O system emphasizes the influence of the concentration mineralizer, the

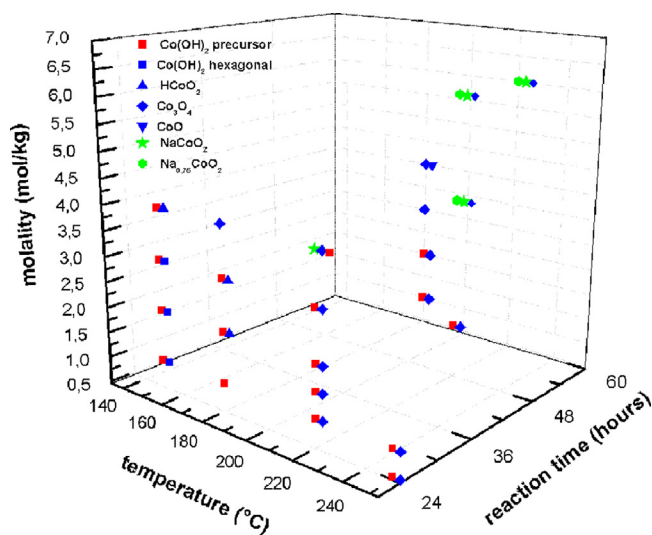


Fig. 1. The stability diagram for Na–Co–H₂O system, for 13 mmol/l Co(OH)₂.

temperature and the reaction time in the formation of desired phase, Na_xCoO₂ phase. The role of the NaOH in the synthesis Na_xCoO₂ phase is to increase the solubility of the metal complexes by increasing the hydroxide concentration and also one of precursors of desired phase. The diagram for Na–Co–H₂O system has shown that optimum yield of Na_xCoO₂ phase occurred if the temperatures vary between 220 °C and 250 °C and respectively, the NaOH molality from 4 mol/kg to 6 mol/kg. As can be seen Na_xCoO₂ phase is a multiphase mixture which consists of Na_{0.75}CoO₂ and NaCoO₂ phases, but Co₃O₄ and Na₂O phases were found to be the coexisting phases. When Na₂O phase are removed completely, Na_xCoO₂ phase disappears and the X-ray pattern is shown only Co₃O₄ phase. A possible explanation could be that non-complexed Co (IV) ions are unstable oxidiser in water and thus Na_xCoO₂ still remains an unstable phase.

The results indicate that the hydrothermal method is useful for preparing layered sodium cobalt oxide and low synthesis conditions determined from the yield diagram for Co–Na–H₂O system open the possibility to obtain Na_xCoO₂ pure stable phase by one step hydrothermal method.

3.2. Hydrothermal synthesis of the three-layered sodium cobaltite

In order to stabilize the Na_{0.6}CoO₂ phase, an extra oxygen content has been introduced in the hydrothermal solution and the influence of the concentration oxidating agent, the temperature and the reaction time on the formation of desired phase has been studied.

The positive effect of the extra oxygen content on high oxidation state of cobalt was observed even at 180 °C, where only 3% hydrogen peroxide has determined the appearance of mixture between Co²⁺ and Co³⁺ ions by comparison with our previous work where it was observed that Co₃O₄ phase is established at 220 °C. The increasing of extra oxygen content (5 % hydrogen peroxide) has been determined the occurrence of the layered sodium cobalt oxide phases, the mixture between Na_{0.75}CoO₂ and NaCoO₂ accomplished by the intermediary phases, Co₃O₄ and CoOOH. As the temperature increases at 220 °C, Co²⁺ is almost completely removed and majority phases have become P3 – Na_{0.6}CoO₂ and CoOOH for 24 h and respectively P3 – Na_{0.6}CoO₂ (JCPDS 01-071-1281, space group: R3m), Na_{0.75}CoO₂ (JCPDS 00-032-1068, space group: C 2/m) and NaCoO₂ (JCPDS 01-070-2030, space group:

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