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A preliminary study on the hydrothermal synthesis of layered cobalt oxides

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Layered sodium cobalt oxide is an attractive magnetic material for thermoelectric applications. The Seebeck coefficent of this material exceeds unity and it shows different types of magnetic behaviour depending on the Na content in Na_xCoO_2. A preliminary study is elaborated for obtaining the layered sodium cobalt oxide materials by hydrothermal synthesis method. In order to discover conditions for the hydrothermal synthesis of Na_xCoO_2 phase, we studied the influence of the concentration mineralizer, the temperature, the reaction time and $Co(OH)_2$ concentration in the formation of desired phase, Na_xCoO_2 phase. From these results, it is encouraging that Na_xCoO_2 pure phase is possibly produced if suitable experimental conditions are chosen. The low temperature and pressure synthesis conditions propose the hydrothermal method that a facile and cheaper preparation method of layered sodium cobalt oxide.

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1. Introduction

Thermoelectric materials are the materials that can convert heat into electric energy. Figure of merit thermoelectric device is given by $Z= S^2 \sigma / k$ where S-Seebeck coefficent, σ - electrical conductivity and k-thermal conductivity. To maximize the thermoelectric figure of merit of a material, a large thermopower (absolute value of the Seebeck coeficient), high electrical conductivity and low thermal conductivity are required.

Layered oxide materials are the new class of materials for thermoelectric applications. It was found that layer-structured oxide $NaCo_2O_4$ was a highly effective thermoelectric material, and the dimensionless figure of merit ZT of single crystal of $NaCo_2O_4$ was shown to exceed unity, which standard value for practical applications [1-2]. The crystal structure of Na_xCoO2 consists in the CdI2-type hexagonal CoO_2 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]. 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 [5-6].

To our knowledge, there have been no reports on layered sodium cobalt oxide prepared by hydrothermal method. Hydrothermal synthesis offers many advantages over conventional and nonconventional ceramic synthesis methods. The low reaction temperature avoid other problems encountered with high temperature processes such a poor stoichiometry control due to volatilization of components [7].

In order to discover conditions for the hydrothermal synthesis of Na_xCoO_2 phase, we studied the influence of the concentration mineralizer, the temperature, the reaction time and $Co(OH)_2$ concentration in the formation of desired phase, Na_xCoO_2 phase.

2. Experimental

All of chemical reagents used in this experimental were of analytical grade. Cobalt(II) hydroxide ($Co(OH)_2$) and sodium hydroxide (NaOH) were purchased from Sigma-Aldrich. Because the solubility product of $Co(OH)_2$;is very less (6×10^{-15}), we experimented with 6.5, 10 and 13 mmol/l of $Co(OH)_2$.

In typical synthesis process, 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 bars in according with PVT diagram of water [8]. Samples were prepared in the temperature range from 150 ºC to 250 ºC, reaction time 24, 48 and 60 hours and 1 - 4 mol/kg of NaOH in an aqueous solution. 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 ºC. The structure of products was determined by powder X-ray diffraction (XRD) using Cu-Kα radiation with (λ=1.5418 Ǻ), in the range 2θ = 5-80°, at room temperature.

3. Results

The role of the NaOH in the synthesis Na_xCoO_2 phase is to increase the solubility of the metal complexes by increasing the hydroxide concentration and also one of precursors of desired phase. Whatever the NaOH amount, at 180°C, no Na_xCoO_2 phase was found. It was observed only the evolution of $Co(OH)_2$ precursor (space group: P-3m1; JCPDS 01-074-1057) to $Co(OH)_2$ hexagonal (unknown space group ; JCPDS 00-001-0357) for the low temperature and NaOH concentration. At 150°C and 4 mol/kg of NaOH, $Co(OH)_2$ hexagonal dissapers and it is replaced by $HCoO_2$. The transformation of $Co(OH)_2$ precursor continues with the increasing the NaOH molality and temperature, $HCoO_2$ becomes the majoritary for 180°C and 3 mol/kg NaOH. The next step of $Co(OH)_2$ evolution was the appearance of mixture between Co^{2+} and Co^{3+} ions, Co_3O_4 phase. It can be observed that Co_3O_4 phase remains stable at 220°C and low molality NaOH.

Na_xCoO_2 phase is built if the temperatures vary between 220 and 250°C and respectively, the NaOH molality from 4 mol/kg to 6 mol/kg. It can be observed that Na_xCoO_2 phase is a multiphase mixture which consists of $Na_{0.75}CoO_2$ and $NaCoO_2$ phases (Fig. 1).

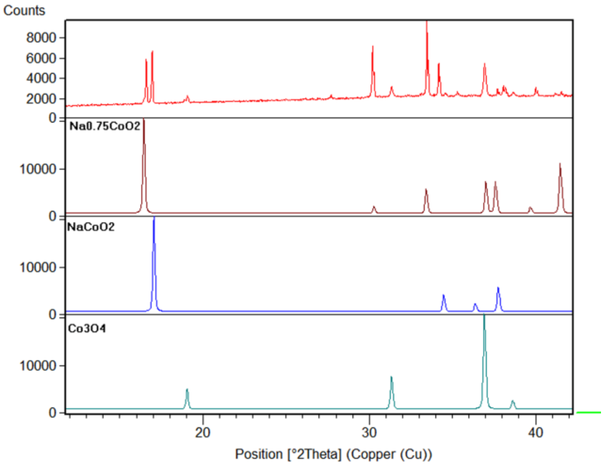

Fig. 1. Room temperature X-ray diffraction pattern of the sample obtained at 220°C, 4 mol/kg NaOH, 13 mmol/l Co(OH)2 and 24 h compared to XRD reference patterns.

In order to find the optimal synthesis conditions of Na_xCoO_2 pure phase and to remove completely Co_3O_4 stable phase, only $Co(OH)_2$ concentration was decreased to 10 mmol/l and respectively, 6.5 mmol/l, the temperature and NaOH molality were kept 220 °C and respectively, 4 mol/kg NaOH. Whatever time reaction (24, 48 and 60 h) and $Co(OH)_2$ concentration, the multiphase mixture which consists of $Na_{0.75}CoO_2$ (space group: C 2/m; JCPDS 00-032-1068), $NaCoO_2$ (space group: R-3m; JCPDS 01-070-2030), Co_3O_4 and Na_2O phases remain. A reducing of Co_3O_4 phase was observed increasing the time reaction, but it was accompanied by CoO phase. The same behavior was observed at 250°C where all phases mentioned above remain stable.

An unexpected result was observed in during of cleaning process. In first stage, the hydrated layered cobalt oxide $Na_{0.342}(H_3O)_{0.238}CoO_2(H_2O)_{1.19}$, with space group P63/mmc is establish (Fig. 2). This phase is very interesting because superconducting properties [9].

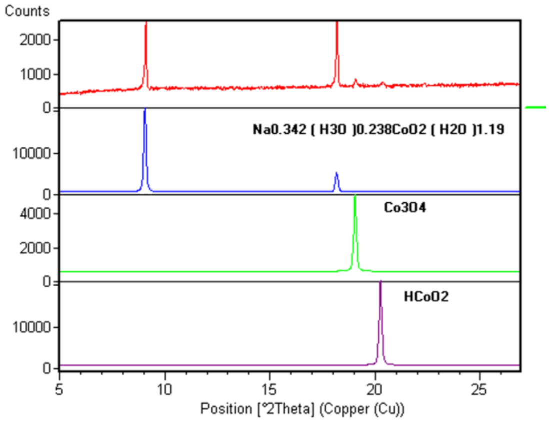

Fig. 2. Room temperature X-ray diffraction pattern of the sample obtained at 220°C, 4 mol/kg NaOH, 13 mmol/l $Co(OH)_2$ and 48 h in during of cleaning process compared to XRD reference patterns.

When Na_2O phase are removed completely, Na_xCoO_2 phase dissapears and the X-ray pattern is shown only Co_3O_4 phase (Fig. 3). It seems that Na_xCoO_2 still remains a instable phase.

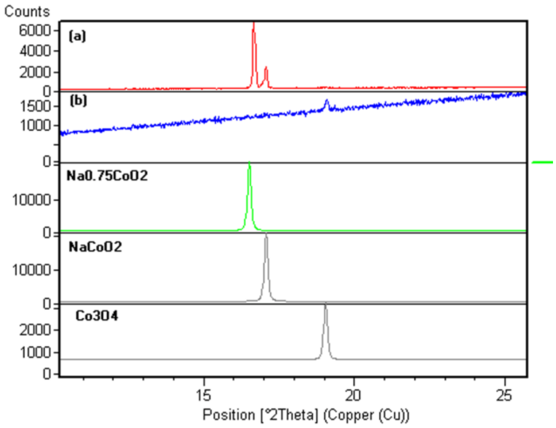

Fig. 3. Room temperature X-ray diffraction patterns of sample obtained at 220°C, 4 mol/kg NaOH, 10 mmol/l $Co(OH)_2$ and 24 h (a) before cleaning process and (b) after cleaning process compared to XRD reference patterns.

4. Discussion

We found that the hydrothermal method is useful for preparing Na_xCoO_2 phase. At low temperature and low molality NaOH, up to 220°C and respectively 4 mol/kg, the evolution of $Co(OH)_2$ precursor can be summarized by the follow reactions:

$$Co(OH)_2+0.25O_2 \rightarrow CoOOH+0.5H_2O \quad (1)$$

$$3CoOOH \rightarrow Co_3O_4+1.5H_2O+0.25O_2 \quad (2)$$

The first layered cobalt oxide phase was observed at 220°C and 4 mol/kg NaOH. In this conditions, the pure phase wasn’t established, layered cobalt oxide phase is a multiphase mixture which consists of $Na_{0.75}CoO_2$ and $NaCoO_2$ phases. It seems that these specific conditions were favored the apparence of high oxidation state Co^{4+} and Co^{3+}. Thus, we propose the hypothesis that aquo Co(III) and Co(IV) and Na(I) hydroxo species have the thermodynamically conditions for the interaction and the layered cobalt oxide phase, Na_xCoO_2 was established.

Also, low synthesis conditions determined from this preliminary study open the possibility of stabilizing a single phase Na_xCoO_2 if extra oxygen content will be introduced in the hydrothermal solution.

5. Conclusion

To summarize, we had first synthesized layered cobalt oxide phase by hydrothermal method. From these results, it is encouraging that Na_xCoO_2 pure phase is possibly produced if suitable experimental conditions are chosen. The low synthesis conditions propose the hydrothermal method that a facile and cheaper preparation method of layered sodium cobalt oxide. In future investigations, our attention will be focused on the find the hydrothermal conditions which allow to obtain a pure and stable Na_xCoO_2 and hydrated layered cobalt oxide.

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