

Thermodynamic properties of stoichiometric lithium cobaltite LiCoO_2



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ABSTRACT

Lithium cobaltite LiCoO_2 was prepared by solid state route and characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), magnetic properties measurement and simultaneous thermal analysis (STA). The heat capacity and enthalpy increments were measured by physical property measurement system (PPMS), differential scanning calorimetry (DSC) and drop calorimetry. The oxygen non-stoichiometry was determined using thermogravimetric measurement (TG). Above room temperature the temperature dependence of the molar heat capacity was derived by simultaneous least squares method from DSC and enthalpy data. The heat capacity was also analyzed in terms of a combined Debye–Einstein model. The molar entropy was evaluated from the low temperature heat capacity data.

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1. Introduction

Lithium cobaltites are widely used as cathode materials in lithium-ion batteries. The unique layered structure of LiCoO_2 enables the formation of lithium deficient oxide $\text{Li}_{1-x}\text{CoO}_2$ during the charging/discharging process. Transport of lithium from LiCoO_2 is accompanied by oxidizing the cobalt from Co^{3+} to Co^{4+} during charging, and conversely by the reduction from Co^{4+} to Co^{3+} during discharging [1–3].

Lithium cobaltite is also an interesting material for its thermoelectric properties. Various high temperature thermoelectric materials have been reported, among them the most suitable candidates seem to be cobalt mixed oxides such as $\text{Ca}_3\text{Co}_4\text{O}_9$ [4–6], $[\text{Bi}_2\text{Sr}_2\text{O}_4][\text{CoO}_2]_{1.85}$, [7] $\text{Bi}_{24+x}\text{Co}_{2-x}\text{O}_{39}$ [8,9], Na_xCoO_2 [10], $\text{Sr}_6\text{Co}_5\text{O}_{15}$ [11], $\text{Bi}_2\text{Sr}_2\text{CoO}_6$ [12] and many others. The first two belong to a group of misfit layered cobaltites, whose structure is composed from two different blocks: rock-salt block and $[\text{CoO}_2]$ block which is isostructural to CdI_2 .

LiCoO_2 has a very similar layered structure exhibiting hexagonal space group $R\text{-}3\text{mH}$, where lithium ions are intercalated between $[\text{CoO}_2]$ blocks [13]. The structure has been analyzed in detail using high-resolution transmission electron microscope (HRTEM) by Shao-Horn et al. [14]. In the structure, lithium can be also

substituted by other ions such as sodium. The Li–Na solid solution member with a composition $\text{Li}_{0.42}\text{Na}_{0.38}\text{CoO}_2$ has been reported by Berthelot et al. [15]. On the other hand cobalt can be substituted by nickel forming $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ [16] or by manganese forming $\text{LiMn}_x\text{Co}_{1-x}\text{O}_2$ [17].

Apart from structural studies also thermoelectric and magnetic properties have been already described in the literature. The impact of lithium composition on the thermoelectric properties of the $\text{Li}_{1-x}\text{CoO}_2$ has been reported by Motohashi et al. [18], Galakhov et al. reported magnetic susceptibility and the valence-band structure of LiCoO_2 [19]. In our paper we focus our study on the thermodynamic properties and oxygen non-stoichiometry of lithium cobaltite. This knowledge will be useful for the calculation of phase equilibria and construction of the T - x_{Li} - p_{O_2} phase diagram in the Li–Co–O system.

2. Experimental

The pure powders of Li_2CO_3 (Aldrich, ACS), and Co_3O_4 (Aldrich, ACS) were weighed and mixed in an agate mortar in ratios corresponding to stoichiometric LiCoO_2 and calcined in a platinum crucible at 1073 K for 12 h. After the calcination the powder was manually reground and homogenized. The powder was then pressed into pellets under the pressure of 300 MPa. The pellets were sintered in air dynamic oxygen atmosphere at 1123 K for 100 h and slowly cooled down (3 K min^{-1}) to ensure the formation of a phase fully saturated by oxygen. The used chemicals and their purities are shown in Table 1.

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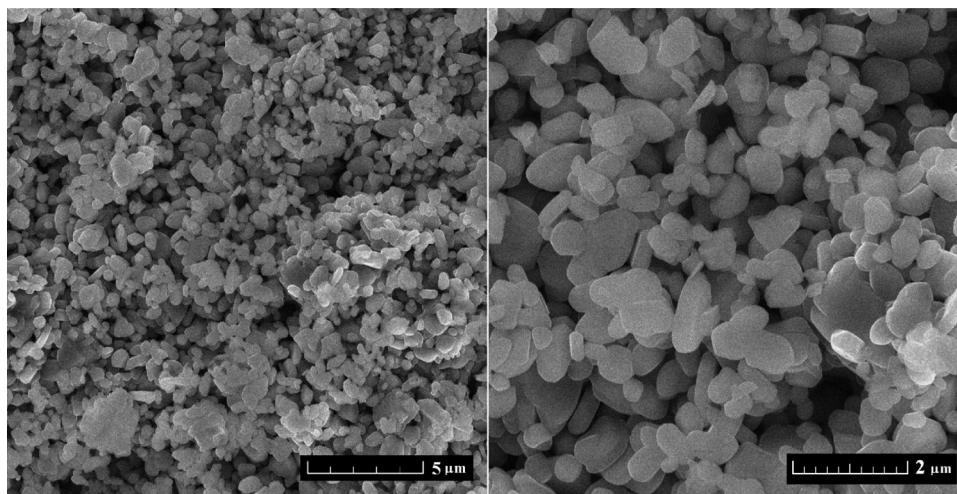


Fig. 1. SEM micrographs of LiCoO_2 . Scale bar is $5\ \mu\text{m}$ (left image) and $2\ \mu\text{m}$ (right image).

Table 1

Used chemicals and their purities, composition of prepared sample and experimental results obtained by XRD.

Used chemicals	Supplier	Purity
Li_2CO_3	Aldrich	>99.9%
Co_3O_4	Aldrich	>99.9%
Sample composition	Used techniques	
	XRD	SEM-EDS
LiCoO_2	single-phase	no impurities

The samples were analyzed by X-ray powder diffraction (XRD). Data were collected at room temperature with Bruker AXS D8 θ - θ powder diffractometer with parafocusing Bragg-Brentano geometry using $\text{CoK}\alpha$ radiation. Rietveld refinement was performed using Full Prof Suite program.

The morphology was investigated by scanning electron microscopy (SEM) with a FEG electron source (Tescan Lyra dual beam microscope). The elemental composition and mapping was performed with energy dispersive spectroscopy (SEM-EDS) analyzer X-Max^N with $20\ \text{mm}^2$ SDD detector from Oxford instruments and software package AZtecEnergy using a Tescan Lyra dual beam microscope with an FEG electron source.

The temperature dependence of magnetic susceptibility ($T=2$ – $300\ \text{K}$, $\mu_0H=0.1\ \text{T}$) and the magnetization curves ($\mu_0H=0$ – $7\ \text{T}$, $T=2$, $5\ \text{K}$) were measured by vibrating sample magnetometer installed in PPMS (Quantum Design, USA) on a small piece of sample pellet ($16.8\ \text{mg}$) under the vibration frequency $60\ \text{Hz}$ and the amplitude $1\ \text{mm}$.

The single-phase sample was measured by simultaneous DTA and TG using Setaram Setsys Evolution from to $1600\ \text{K}$ to determine the temperature of melting and oxygen non-stoichiometry. The heating rate was set to $5\ \text{K}\ \text{min}^{-1}$ and the measurement was carried out in dynamic air atmosphere ($50\ \text{cm}^3\ \text{min}^{-1}$) where the value of $p_{\text{O}_2}/p^0=0.21$ ($p^0=101.3\ \text{kPa}$).

The PPMS equipment 9T, Evercool-type (Quantum Design, USA) was used for the heat capacity measurements in the low-temperature region. The measurements were performed by the relaxation method with fully automatic procedure under high vacuum (pressure $\sim 10^{-2}\ \text{Pa}$) to avoid heat losses through the exchange gas. The sample was mounted to a calorimeter platform with cryogenic grease Apiezon N (supplied by Quantum Design). A blank sample holder with the Apiezon only was measured prior to the sample itself in the temperature range 2 – $257\ \text{K}$ to obtain the

background data. Then the sample plate was attached to the calorimeter platform and the measurement was repeated using the same temperature program. The sample heat capacity was then obtained as a difference between the two data sets. The manufacturer claims the accuracy of this measurement better than 2%; the control measurement of the copper sample (99.999% purity) confirmed it in the temperature range 50 – $250\ \text{K}$. Kennedy et al. reported the accuracy of heat capacity measurements on single crystal sapphire and copper less than 5% and 1% for temperature intervals $0.7\ \text{K}<T<5\ \text{K}$ and $5\ \text{K}<T<300\ \text{K}$, respectively [20]. However, the precision of the measurement strongly depends on the thermal coupling between the sample and the calorimeter platform. Due to unavoidable porosity of the sample plate this coupling is rapidly getting worse as the temperature raises above $270\ \text{K}$ and Apiezon diffuses into the porous sample. Consequently, the uncertainty of the obtained data tends to be larger. So the relative standard uncertainty 2% was considered in this work.

Micro DSC III calorimeter (Setaram, France) was used for the heat capacity determination in the temperature range of 261 – $358\ \text{K}$. The heat capacity was measured in the incremental temperature scanning mode consisting of a number of $5\ \text{K}$ steps (heating rate $0.3\ \text{K}\ \text{min}^{-1}$) followed by the isothermal delays of $2600\ \text{s}$. Synthetic sapphire, NIST Standard reference material No. 720, was used as the reference. The relative standard uncertainty of the heat capacity measurements is estimated to be 1%.

Enthalpy increments determination was carried out by drop method using high temperature calorimeter Multi HTC 96 (Setaram, France). All measurements were performed in air by the alternating dropping of a reference material (small pieces of synthetic sapphire, NIST Standard reference material No. 720) and of a sample (small pieces of pellets) being initially held at room temperature, through a lock into the working cell of the preheated calorimeter in a following sequence: standard – sample – standard – sample – standard. Endothermic effects are detected and the relevant heat content of the dropped specimen was evaluated from the integrated peak area. The measurements were performed at temperatures $573\ \text{K}$ to $1273\ \text{K}$ on samples of 80 – $120\ \text{mg}$, which provide similar thermal effect as the reference specimens. The delays between two subsequent drops were $20\ \text{min}$ to stabilize the heat flow. To check the accuracy of measurement, the enthalpy increments of platinum in the temperature range 770 – $1370\ \text{K}$ were measured first and compared with published reference values [21]. The relative standard uncertainty was 3%.

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