

Sodium Cobalt Oxide as Functional Thermoelectric Material

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Abstract.

Cobaltite compounds with a layered structure have a functional properties; LiCoO_2 as electrode and Na_xCoO_2 as thermoelectric material. In recent years they have been extensive studied as new electroceramic materials [1-2]. Na_xCoO_2 for instance was discovered to possess a very high electric conductivity and large Seebeck coefficient.

The great ability of cobalt to adopt various oxidation state has influenced on the physical and chemical properties and specially on the thermoelectrical properties. In this respect determination of cobalt valence is interest for monitoring of quality of samples.

Na_xCoO_2 powder has been prepared by the solid state reaction of Co_3O_4 and carbonate on multi-step calcination and presintering process. Products were investigated by XRD and TG/DTA analysis. The content of cobalt on different oxidation state in sodium cobaltites were measured with three chemical methods: iodometric, complexometric with Cr^{3+} and with EDTA. Results determined by different redox reaction (iodometric, chromatic and H_2 reduction) were in a good accordance. The all samples content of Co^{3+} and Co^{4+} , some sample (second quality samples) also Co^{2+} . The ratio of $\text{Co}^{3+}/\text{Co}^{4+}$ are close between 1,1 and 1,8. These values are correlated with electrical properties [3].

Na_xCoO_2 exhibits promise good thermoelectric properties: thermopower up to $150 \mu\text{V/K}$, electrical conductivity 300 S/cm and thermal conductivity up to $2 \text{ W/m}^*\text{K}$. The Pb substituted samples shows enhancement of the thermoelectric properties [4].

Introduction

Thermoelectric power generation, direct energy conversion from heat to electrical power, has very good perspectives in applications, if high-temperature heat source makes the output power and efficiency raised by large temperature difference.

Cobaltites with delafossite-type structures show good chemical stability up to high temperature combined with a large Seebeck coefficient and small resistivity as well as thermal conductivity. Four of these cobaltites: Na_xCoO_2 , $\text{Ca}_2\text{Co}_2\text{O}_5$, $\text{Ca}_3\text{Co}_4\text{O}_9$ and $\text{Ca}_3\text{Co}_2\text{O}_6$ are known to be good thermoelectrics, because of their metallic conductivities and high thermoelectric power. These layered cobaltites show a common structural component: the CoO_2 planes, in which a two-dimensional-triangular lattice of Co ions is formed by a network of edge-sharing CoO_6 octahedra. The attractive physical properties of layered cobaltates are strongly dependent upon overall oxygen content as well as local, or longer range, ordering. Electronic and ionic conductivity is known to be strongly affected by the related $\text{Co}^{3+}/\text{Co}^{4+}$ ratio and distribution.

Progress in the application of thermoelectric cobaltites for thermogenerator is due to the improvement of good quality materials. Manufacturing of technically applicable thermoelectric cobaltites requires well-defined preparation technique to obtain chemical homogen, dense ceramic bulk materials.

Preparation and characterization of sodium cobaltate

Polycrystalline samples of Na_xCoO_2 were prepared by a conventional solid-state reaction. Starting materials, Na_2CO_3 (Merck) and Co_3O_4 (Chempur) were mixed in a molar ratio of Na:Co = 0,6-1,0 : 1, calcined at 750 °C for 12 h, repeated mixed and sintered at 800 °C for 12 h. Black homogeneity powder was obtained. After sintering the samples consisted only Na_xCoO_2 phase for the starting x-value 0,8-1,0 and with small amount of Co_3O_4 for the starting x-value 0,6-0,7 (fig.1).

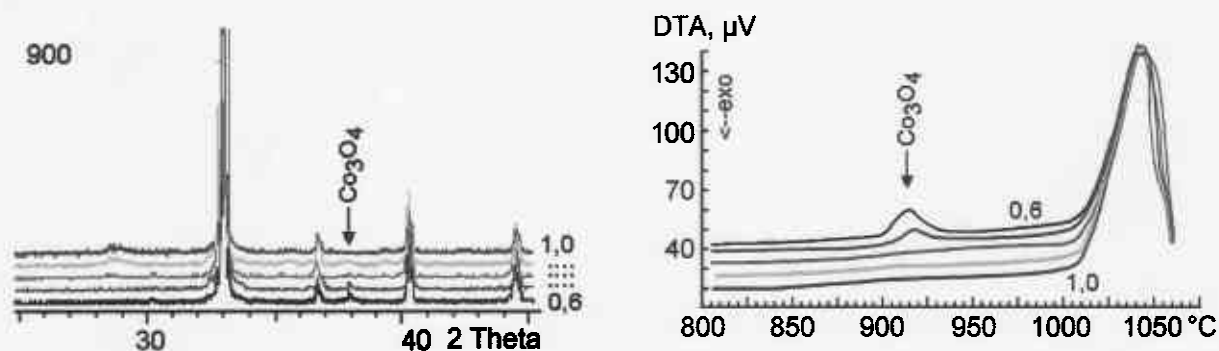


Fig.1. X-ray diffraction and DTA curves of the samples Na_xCoO_2 for starting x-value between 0,6 and 1,0. Sintering temperature 900 °C, duration 12 h.

The stability of Na_xCoO_2 (starting x-value 0,8) was investigated by thermal analysis (fig.2). Na_xCoO_2 was not stable at the temperature higher than 1000°C and showed decomposition and melting. The endothermic reaction was observed at about 1000°C , the weight loss during this step can be attributed to the oxygen. The thermograph for the pure phase did not show peaks from Co_3O_4 (main impurities of cobaltites). These TG curve indicated a rapid loss of weight at round 1000°C (about $\Delta m=8,9\%$), which can be attributed to the desorption of oxygen and a sodium evaporation from the Na_xCoO_2 phase during the heating process. These value of weight loss to correspond of $x=0,78$ (for ignoring of volatilization of the sodium).

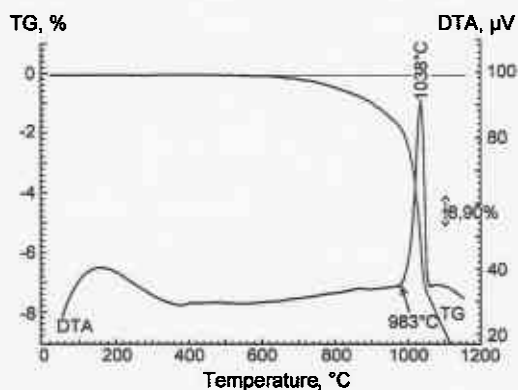


Fig.2 Thermograph of pure Na_xCoO_2 sample Sintering temperature 900°C , duration 12 h

It can be seen that decomposition and melting process is complete at a temperature close to the endothermic peak at 983°C as determined by the DTA trace. The TG/DTA data of these sample show that Na_xCoO_2 were single phase and that from XRD data had the hexagonal γ structure.

Thermoelectric properties of Na_xCoO_2

After intermediate milling and palletizing, the green body was sintered at 900°C . The samples containing various amounts of Na, because of Na evaporate during firing of pellets. The AAS analysis was used for quantitative determination of sodium. For example: the pellets sintered at 900°C for 12 h to contain 14,4 % Na ($\text{Na}_{0,66}\text{CoO}_2$), after 24 h 11,4 % Na ($\text{Na}_{0,51}\text{CoO}_2$), after 168 h 12,1 % Na ($\text{Na}_{0,53}\text{CoO}_2$), and after 336 h only 10,2 % Na ($\text{Na}_{0,45}\text{CoO}_2$).

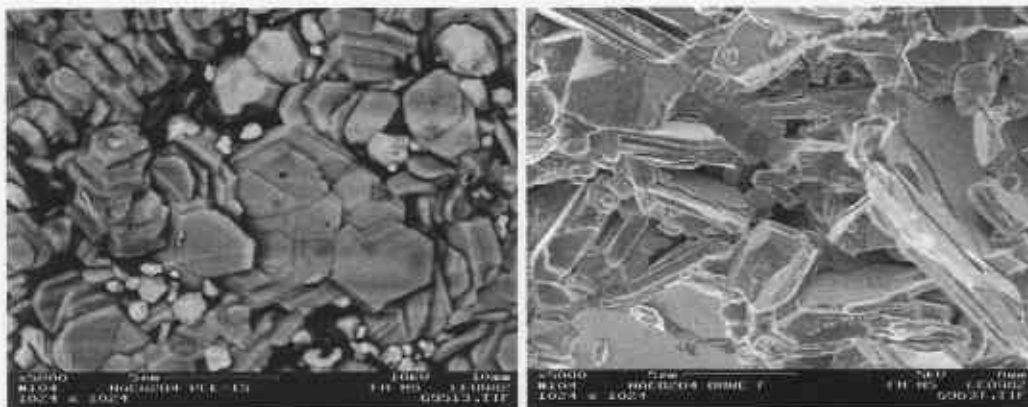


Fig.3 Surface and breach of the Na_xCoO_2 tablet sintered at 900 for 12 h

This sample consists of plate-like Na_xCoO_2 grains, where some Co_3O_4 round particles were trapped. The larger plate-like grains were produced as a results of significant grain growth with duration time [5,6]. Unfortunately with duration of sintering time samples losses of sodium.

The functional properties of Na_xCoO_2 - ceramics are development at high temperature. The thermopower shown in fig.4 is less obviously affected by cobaltite modification and oxygen content. α -, α' - and γ -phase exhibited the same characteristic temperature dependence $S(T)$ with an nearly linearity increasing $S(T)$ of the γ -phase and broad minima in $S(T)$ of the α - and α' -phases [5]. The positive Seebeck coefficient indicates holes as the main charge carriers for each sample regardless of composition and crystal structure. The Seebeck coefficient generally increased with the rising Na content from γ - via α' to α -phase. This succession is correlated to the decrease of the electrical conductivity.

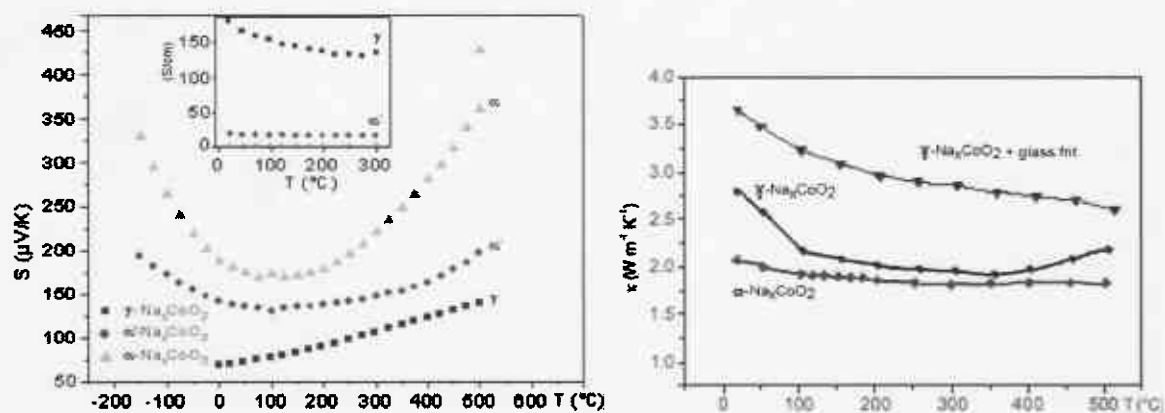


Fig.4. Temperature dependent Seebeck coefficient in $\mu\text{V/K}$ with electrical conductivity in S/cm and thermal conductivity κ in $\text{W/m}^2\text{K}$ of the modifications Na_xCoO_2

It is evident that the Na content x affected of the electrical conductivity regardless of the oxidation states of Co in cobaltite. The $\text{Co}^{3+}/\text{Co}^{4+}$ ratio is of 1,8 in γ -phase and in α -phase ($x \approx 1$) oxidation state resulting of +3 for Co. Reducing x in Na_xCoO_2 increases the average oxidation state of Co and increase the electrical conductivity (creates defect electrons in the valence band [4]). The change of electrical conductivity are measured for doped samples (tab.1)

Tab. 1. Electrical conductivity $\sigma(25^\circ\text{C})$ of $\text{Na}_x\text{Co}_{0,95}\text{M}_{0,05}\text{O}_2$ samples

M	Ti	V	Cr	Mo	W	Fe	Ni	Cu	Al	Ga	Pb
σ (S/cm)	15	110	150	220	170	115	200	270	175	135	210

The thermal conductivity of different phases of Na_xCoO_2 are similar (fig.4). After addition of glass frit the thermal conductivity was significantly increased (and porosity decreased).

Na_xCoO_2 ceramics with big grains (sintering duration of 7 day) exhibits electrical conductivity 300 S/cm and thermal conductivity up to 2 W/mK. The Pb substituted samples shows enhancement of the thermoelectric properties [6].

Summarizes the measured values of the thermopower for Na_xCoO_2 samples and comparison with the partial substituted one ($\text{Na}_x\text{Co}_{1-y}\text{M}_y\text{O}_2$) shows that the partial substitution of Co by Pb enhanced significantly the ZT of γ - $\text{Na}_{0,5}\text{CoO}_2$ mostly due to on increased conductivity and reduced thermal conductivity

Tab.2. Seebeck coefficient and ZT- values of Na_xCoO_2 samples

composition	S(500°C), $\mu\text{V/K}$	ZT(500°C)
$\text{Na}_{0,5}\text{CoO}_2$ (γ -phase)	134	0,115
$\text{Na}_{0,9}\text{CoO}_2$ (α -phase)	360	0,026
$\text{Na}_{0,5}\text{Co}_{0,95}\text{Pb}_{0,05}\text{O}_2$ (γ -phase)	106	0,075
$\text{Na}_{0,95}\text{Co}_{0,95}\text{Pb}_{0,05}\text{O}_2$ (α -phase)	270	0,130 (300°C)

Conclusion

Ceramic thermoelectric material with composition of Na_xCoO_2 showed structure with plate-like grains. These materials are different Na content, because sodium evaporated at high temperatures during of formation of this compounds and during of sintering of ceramic. The plate-like grains grew with sintering duration and the electrical conductivity was high. Similar effect were obtained by doping with Pb. These ceramic shows the thermoelectric figure of merit $\text{ZT}(500^\circ\text{C}) > 0,1$.

Literature

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