# Chemical route for monitoring synthesis of cobaltites

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**Abstract**

Study on the determination of cobalt on higher oxidation states is presented. Chemical methods were used which, because of specific properties of reagents, gave possibility for determining $Co^{3+}$ in the presence of $Co^{4+}$ in sodium and calcium cobaltites.

The content of cobalt on different oxidation states in calcium and sodium thermoelectric cobaltites was measured and the results are correlated with the electrical properties.

## 1. Introduction

Oxide ceramics, due to their high stability at high temperature in air, easy manufacture and low cost, have attracted much attention as thermoelectric materials. Among the metal oxides, Co-based oxides, with a layered structure such as $Na_{0,75}CoO_2$, $NaCo_2O_4$, $Ca_2Co_2O_5$ and $Ca_3Co_4O_9$ have been reported as particularly strong candidates [1,2]. All these materials show a large thermoelectric power simultaneously accompanied by a low resistivity. The reason of such behaviour is still discussed. Determination of the thermoelectric power of has indicated that the oxidation state of cobalt is one of the most important factor influencing thermoelectric properties. At present the value of the oxidation state of cobalt is described as an average of all oxidation states of cobalt present in cobaltite [4]; in literature one can find that this value directly depends on preparation methods and XRD, DTA/TG seem to be insufficient as material characterisation methods. It is believed that separate determination of cobalt on each oxidation state lets for controlling cobaltites processing. In this paper study on the determination of cobalt on higher oxidation state is presented. Chemical methods were used which, because of specific properties of reagents, gave possibility for determining $Co^{3+}$ in the presence of $Co^{4+}$ in such materials.

Results of determinations are correlated with the electrical properties.

## 2. Experimental

Sodium and calcium cobaltites were prepared by solid state reaction;

Two samples with the nominal composition of $Na_{0.75}CoO_2$ as well as the samples with starting Ca:Co=1:1 and Ca:Co= 3:4 cation ratio were prepared. Cobalt (II,III) oxide and sodium or calcium carbonates (used as a starting materials) in a molar ratio corresponding to the nominal composition of $Na_{0,75}CoO_2$, $Ca_2Co_2O_5$ or $Ca_3Co_4O_9$ were mixed in agate mill during 1h with addition of acetone. The mixtures were then calcined at 800°C (for sodium cobaltites) and 850°C (for calcium cobaltites) during 16 hours in air in the oven. After that, resulted powders were mixed in agate mill for the second time, during 1h with addition of acetone. Mixtures were then pressed into tablets and sintered at 850°C (for sodium cobaltites) and 900°C (for calcium cobaltates) during 12 - 168h in the oven using oxygen or air atmosphere.

Synthesis was controlled by XRD and DTA/TG. Chemical methods for analysis of total cobalt content, $Co^{4+}$, $Co^{3+}$ and $Co^{2+}$ content were elaborated. Determinations were carrying out on various cobaltite samples. Results from the determinations are shown in the Table 1. Finally, measurements of the electrical resistivity were applied to the sintered tablets .

### 2.1. Determination of $Co^{3+}$ content

*Samples preparation and determination procedure:*
10mg of the cobaltite sample was put into the beaker; 10ml of 0,25M EDTA and 0,3ml of 2M $H_2SO_4$ were added. Solution was heated till complete dissolving of the sample. Next, the solution was transferred to the 50ml volumetric flask. The absorbance of the solution was measured at λ 534nm against water and cobalt content calculated. Molar absorptivity at λ 534nm =$2.94 \cdot 10^2$.

### 2.2 Indirect determination of $Co^{4+}$ content

In the first step ”oxidation factor” calculated on the assumption that only CoIII is present in the sample and only 1 electron involved in reduction of CoIII/CoII is found. The amount of CoIII determined according to the procedure described in 2.3.2. is subtracted from this value. The excess which corresponds to CoIV content is divided by two, due to the number of electrons involved in CoIV/CoII reduction.

Determination of ”oxidation factor” for cobaltite samples was carried out by two independent methods:

a) Oxidation of $Cr^{3+}$ to $Cr_2O_7^{2-}$ by Co(III) and Co(IV) present in cobaltite samples, followed by spectrophotometric determination of dichromate ions content at λ 350nm

*Samples preparation and determination procedure:*
10mg of the cobaltite sample were put into the beaker, 20ml of chromium and potassium sulphate solution ($Cr^{3+}$ concentration equal to 1mg/ml) were added. The mixture was then heated and stirred till the sample was completely dissolved. The solution was transferred to 25ml volumetric flask. Absorbance of solutions was measured at λ 350nm against water and oxidation factor was calculated. Molar absorptivity $\varepsilon = 7,5 \cdot 10^2$[5].

b) Oxidation of $I^-$ to $I_2$ followed by titration with $Na_2S_2O_3$

*Samples preparation and determination procedure:*50mg of the cobaltite sample were put into the beaker, 10 ml of KI and 5ml of concentrated HCl solution were added. The mixture was left in the dark place to complete dissolution and then it was titrated with 0,1M sodium thiosulphate in the presence of starch as an indicator.

### 2.3. Determination of the content of $Co^{2+}$, existing in the form of free CoO or Co(OH)

*Samples preparation and determination procedure:*
100 mg of the cobaltite sample was put into the beaker, 30 ml of Franky`s reagent was added. The mixture was stirred at the boiling temperature for 1h, then it was filtered, next 20ml of 25M EDTA and 0,5g of $KIO_4$ were added. The mixture was heated for 10min to achieve colour development and then it was transferred to the 50ml volumetric flask. The absorbance of the solution was measured at λ 534nm against water and cobalt content calculated as in 2.1.

### 2.4. Measurements of the electrical resistivity

Measurements of the electrical resistivity were applied to the tablets of all presented cobaltite samples. Having the same and constant intensity (100mA), a voltage was measured for every sample. Measurements were made at the room temperature. Next, using dimensions of samples and received value of voltage – the electrical resistivity was calculated for every sample.

## 3. Results and discussion

Cobalt (III) forms a red coloured complex of high stability with EDTA in a weak acid solution. pK value given in the literature [6] equals to 40,6. It is the most stable complex which EDTA as a ligand forms with metal ions. Sodium and calcium cobaltites dissolve easily in EDTA solution. Resulting red colour of the solution indicates that CoIII present in materials under investigation forms complex with this ligand, which can be used for CoIII quantification. CoII forms less stable complex of much lower sensitivity and do not contribute to the absorbance value at the maximum wavelength of $Co^{3+}$ complex ($\lambda$ = 534nm).

Cobalt (III) and cobalt (IV) can undergo redox reactions. Standard redox potential of $Co^{3+}/Co^{2+}$ couple is very high and equals 1.84V [6] what indicates that the reactions with $Cr^{3+}$ and $I^-$ can go towards oxidation to $Cr_2O_7^{2-}$ and $I_2$ respectively (E° [$Cr_2O_7^{2}/Cr^{3+}$] = 1.33V[6]; E° [$I_2/I^-$] = 0.536V[6])

Sodium and calcium cobaltites dissolve in acid solutions of $I^-$ with liberation of free iodine in amount equivalent to Co(III) and Co(IV) present in the samples, what is frequently used in analysis of various materials [4]. In materials containing CoIII and CoIV the following reactions can be expected:

Reactions of $Co^{3+}$ with $I^-$:
$Co^{3+} + 1e \rightarrow Co^{2+}$
$2I^- - 2e \rightarrow I_2$
$2Co^{3+} + 2I^- \rightarrow I_2 + 2Co^{2+}$

Reactions of $Co^{4+}$ with $I^-$:
$Co^{4+} + 2e \rightarrow Co^{2+}$
$2I^- - 2e \rightarrow I_2$
$2Co^{4+} + 4I^- \rightarrow 2I_2 + 2\,Co^{2+}$

Titration reactions:

$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$
The ratio of $Co^{3+}/S_2O_3^{2-}$ = 1:1

$2I_2 + 4S_2O_3^{2-} \rightarrow 2S_4O_6^{2-} + 4I^-$
The ratio of $Co^{4+}/S_2O_3^{2-}$ = 1:2

Results obtained from titration analysis cannot differentiate between $Co^{3+}$ and $Co^{4+}$ content. They can be used for the determination of "oxidation factor". In this case the assumption is made that in the sample exists only $Co^{3+}$ which consumes 1 electron per 1 ion. Calculation based on the volume of standard thiosulphate solution used for the determination of liberated in redox reaction iodine will give the content of cobalt on higher oxidation states recalculated as $Co^{3+}$.

To asses the $Co^{4+}$ content it is necessary to subtract the $Co^{3+}$ amount determined separately as $Co^{3+}$-EDTA complex from the oxidation factor. The obtained difference divided by 2 (number of consumed electrons by $Co^{4+}$) will give the content of $Co^{4+}$ in the sample.

The difference in standard redox potential indicates that $Co^{3+}$ and $Co^{4+}$ ions can oxidize $Cr^{3+}$ ions according to the possible reactions:

Reactions of $Co^{3+}$ with $Cr^{3+}$:
$Co^{3+} + 1e \rightarrow Co^{2+}$
$2Cr^{3+} - 6e + 7H_2O \rightarrow Cr_2O_7^{2-} + 14\,H^+$
$6Co^{3+} + 2Cr^{3+} + 7H_2O \rightarrow Cr_2O_7^{2-} + 6Co^{2+} + 14H^+$
The ratio of $Co^{3+}/Cr_2O_7^{2-}$ = 6: 1

Reactions of $Co^{4+}$ with $Cr^{3+}$:
$Co^{4+} + 2e \rightarrow Co^{2+}$
$2Cr^{3+} - 6e + 7H_2O \rightarrow Cr_2O_7^{2-} + 14\,H^+$

$$3Co^{4+} + 2Cr^{3+} + 7H_2O \rightarrow Cr_2O_7^{2-} + 3Co^{2+} + 14H^+$$

The ratio of $Co^{3+}/Cr_2O_7^{2-} = 3:1$

In Fig.1 absorption spectra of $K_2Cr_2O_7$ ($Cr^{6+}$) (curve 1) and $Cr^{3+}$ 1mg/ml (curve 2) in UV-Vis range are presented. At $\lambda$=350nm the absorbance maximum of dichromate meets the minimum in $Cr^{3+}$ spectrum. This wavelength can be applied for the determination of dichromate forming in the reaction of $Co^{3+}$ and $Co^{4+}$ ions with $Cr^{3+}$.

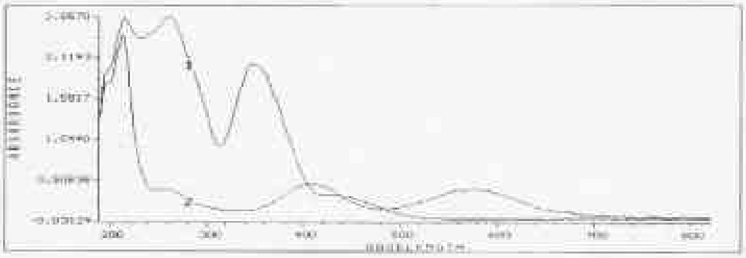


*Fig1: Curve 1- absorption spectra of dichromate standard sample; Curve2- absorption spectra of $Cr^{3+}$ standard sample*

In Fig. 2 the absorption spectra of calcium cobaltite sample after reaction with $Cr^{3+}$(curve1), and standard sample of chromium (III) of concentration 1mg/ml (curve 2) are presented. The well shaped $Cr_2O_7^{2-}$ absorption band is seen. The absorbance value can be applied for the determination of "oxidation factor" recalculated as $Co^{3+}$ content similarly to the aforementioned iodometry.

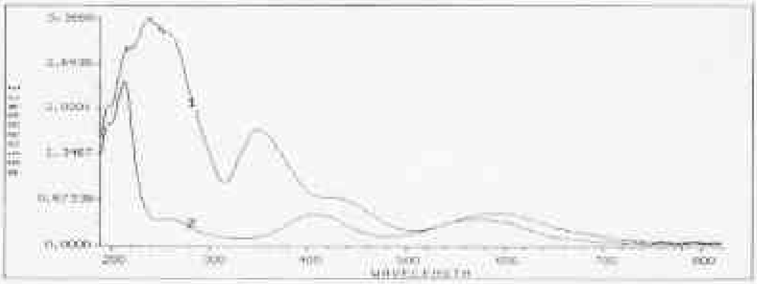
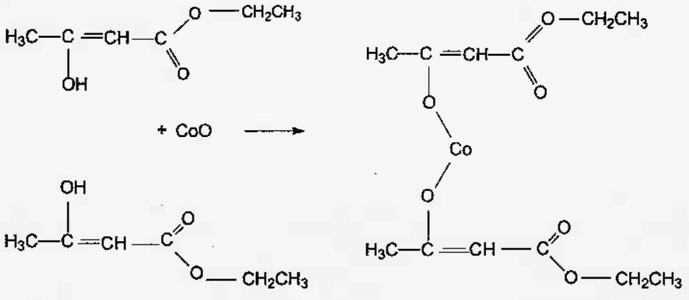


*Fig2: Curve 1- absorption spectra of calcium cobaltite sample after reaction with $Cr^{3+}$; Curve2- absorption spectra of $Cr^{3+}$ standard sample*

In carried out analysis of sodium and calcium cobaltites the good accordance between oxidation factors determined by both redox reactions (iodometry and chromatometry) is noticed (table 1, columns 4 and 6).

Samples of cobaltites can contain free CoO phase. Our investigations revealed that it reacts similarly to CaO with Franky's reagent (ethyl acetylacetate in the presence of isobutyl alcohol and ethyl ether mixed in the volume ratio 3:20:5). The possible reaction goes according to the equation:



The content of $Co^{2+}$ in analysed materials was determined in filtrates obtained as a result of the extraction. EDTA was added to form a complex with Co(II) which was subsequently oxidized with $KIO_4$ to red Co(III)-EDTA complex and measured spectrophotometrically . Results of all analyses are shown in Table 1.

*Table 1: Results of determinations of cobalt on different oxidation states and total cobalt content*

| **sample** | **Co from CoO or $Co(OH)_2$ %** | **$Co^{3+}$ EDTA %** | **oxidation factor $Cr^{3+}$** | **$Co^{4+}$ Cr %** | **oxidation factor J** | **$Co^{4+}$ J %** | **$\sum$ Co SCN %** |
|---|---|---|---|---|---|---|---|
| **$Na_{0,75}CoO_2$**<br>1 | **1,8**<br>±0,2 | **22,9**<br>±0,5 | **62,2**<br>±1,1 | **19,7**<br>±1,1 | **62,1**<br>±0,5 | **19,6**<br>±0,5 | **44,5**<br>±0,6 |
| **$Na_{0,75}CoO_2$**<br>2 | **1,5**<br>±0,2 | **28,8**<br>±0,5 | **66,9**<br>±0,5 | **19,0**<br>±0,5 | **67,0**<br>±0,4 | **19,1**<br>±0,4 | **44,6**<br>±0,5 |
| **$Ca_2Co_2O_5$**<br>1 | **2**<br>±0,5 | **24,1**<br>±0,1 | **45,4**<br>±1,4 | **10,7**<br>±1,4 | **42,8**<br>±0,6 | **9,4**<br>±0,6 | **38,4**<br>±0,2 |
| **$Ca_2Co_2O_5$**<br>2 | **-** | **21,9**<br>±0,5 | **50,2**<br>±0,6 | **14,1**<br>±0,6 | **49,2**<br>±0,5 | **13,6**<br>±0,5 | **42,0**<br>±0,5 |
| **$Ca_3Co_4O_9$**<br>1 | **0,8**<br>±0,2 | **24,6**<br>±0,5 | **56,6**<br>±0,2 | **16**<br>±0,2 | **56,1** | **15,7**<br>±0,2 | **43,8**<br>±0,2 |
| **$Ca_3Co_4O_9$**<br>2 | **1**<br>±0,3 | **29,4**<br>±0,5 | **45,9**<br>±0,5 | **8,25**<br>±0,5 | **46,16**<br>±0,5 | **8,38**<br>±0,5 | **45,9**<br>±0,2 |

The values received from the determination of cobalt on different oxidation state were correlated with the values of electrical resistivity. The results are shown on a Fig. 3 and 4 .

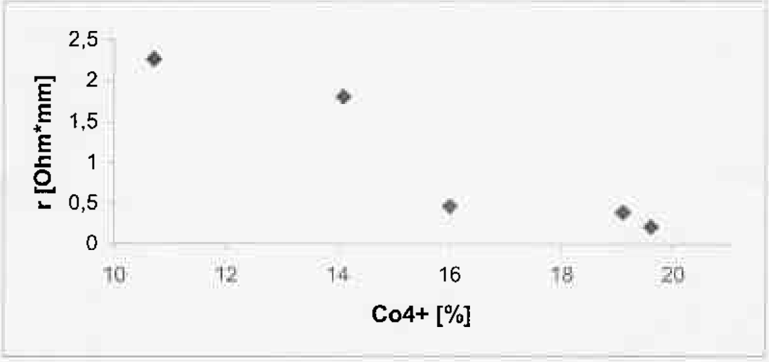


*Fig.3. Relationship between the Co4+ content and the electrical resistivity for different cobaltite samples*

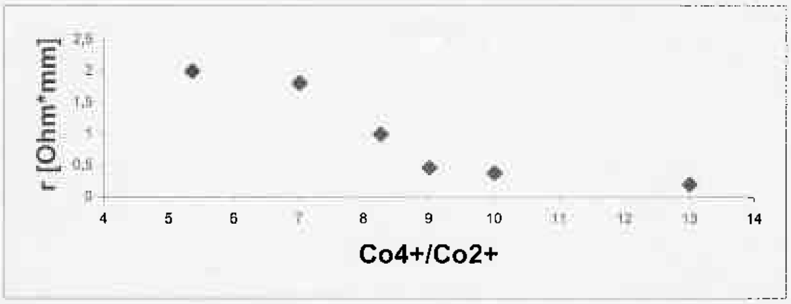


*Fig.4. Relationship between Co4+/Co2+ ratio and the value of electrical conductivity for different cobaltite samples.*

XRD study confirmed that Presented .cobaltites were the main phase in the examined materials while DTA/TG examination revealed small amount of $Co^{2+}$ in some of the tested specimens. None of that method could give quantitative figures for relation between thermoelectric properties and material composition. Presented results from the analytical determinations show that the total content of cobalt in all measured samples is lower than "oxidation factor" determined by two independent redox methods. The existence of the excess value proves occurrence of $Co^{4+}$ form in synthesized materials. The discrepancy between iodometry and chromatometry is in most cases within the determination error. Obtained results indicate that spectrophotometric method with $Co^{3+}$-EDTA complex formation combined with one of the described redox method can be successfully applied for the simultaneous determination of cobalt (III) and cobalt (IV) in sodium and calcium thermoelectric cobalt oxides. The sum of Co content at various oxidation states is always lower than determined independently total cobalt content. It is assumed that the small amount of $Co^{2+}$ could be present in cobaltites network; in that case it can not be determined by the elaborated method.

Samples presented in a Table 1 show different $Co^{4+}$ content made by differences in the calcination processes. Results which are presented on Fig 3 and 4 show, that the electrical resistivity strongly depends on the $Co^{4+}$ content and that relation is independent on the kind of cations in cobaltites (Na or Ca). With increasing of $Co^{4+}$ content in the cobaltite samples their electrical resistivity decrease. If $Co^{4+}$ content is low then resistivity of the material could be also influenced by Co4+/Co2+ ratio (Fig.4)

## Conclusions:

It has been found that chemical analysis of dissolved cobaltites could be successfully applied for determination of cobalt fraction on various oxidation states. It is the first method suitable for searching relation between cobalt oxide based material composition and its thermoelectric behaviour. By changing parameters of cobaltite synthesis Co4+ content could be influenced. Proposed procedures are quick, simple , cheap and can be applied for monitoring synthesis of cobaltites and prediction thermoelectric properties on the basis of $Co^{4+}$ content.

## Literature

1. W. Shin, N. Murayama, K. Ikeda, S. Sago, Oxide Thermoelectrics (K. Kaumoto, I. Terasaki, N. Murayama, Eds.), 2002, 193-211
2. J. Plewa, A. Mrotzek, E. Müller, H. Altenburg, Solid State Phenomena **90-91** (2003) 405
3. M. Sopicka-Lizer, .P. Smaczyński, K. Kozłowska, E. Bobrowska-Grzesik, J. Plewa:"*Preparation and characterization of calcium cobaltite for thermoelectric applications*", Electroceramics IX
4. M. Karpinnen, M. Matvejeff, K. Salomaki, H. Yamauchi, J. Mater. Chem. 12 (2002) 1761
5. Z.Marczenko, M.Balcerzak, "Spektrofotometryczne metody w analizie nieorganicznej ", PWN Warszawa 1998
6. "Poradnik chemika analityka" tom1 " Dane fizykochemiczne, analiza chemiczna", WNT Warszawa 1989