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ASSESSMENT OF Co(II), Co(III) AND Co(IV) CONTENT IN THERMOELECTRIC COBALTITES

OZNACZANIE ZAWARTOŚCI Co(II), Co(III) I Co(IV) W KOBALTANACH WYKAZUJĄCYCH WŁASNOŚCI TERMOELEKTRYCZNE

The precise content of cobalt at a given oxidation state in layered sodium or calcium cobaltites is crucial for their thermoelectric performance and stability at elevated temperature. The paper presents results of searching for an effective method of measuring cobalt ions concentration coexisting at various oxidation state in a solid state. Application of the specific properties of reagents gave possibility to determine Co^{3+} concentration in the presence of Co^{4+} by the wet chemical methods. The accuracy and usefulness of the method was checked by comparison of the results from independent measurement of the total cobalt content and sum of the cobalt concentration at various oxidation state. It has been found that separate concentration of cobalt at a various valence state can be precisely measured if no Co_3O_4 was present in the synthesized powders.

Dokładne oznaczenie zawartości kobaltu na danym stopniu utlenienia w warstwowych kobaltanach sodowych lub wapniowych ma zasadnicze znaczenie dla ich sprawności jako materiału termoelektrycznego oraz stabilności w podwyższonej temperaturze. Artykuł przedstawia wyniki badań nad znalezieniem skutecznej metody oznaczania stężenia jonów kobaltu występujących obok siebie na różnym stopniu utlenienia w stanie stałym. Wykorzystanie szczególnych właściwości reagentów umożliwiło oznaczenie stężenia Co^{3+} obok Co^{4+} metodą analizy w fazie ciekłej. Dokładność i powtarzalność metody została potwierdzona przez porównanie wyników niezależnych pomiarów całkowitej zawartości kobaltu i sumowania zawartości kobaltu na różnych stopniach utlenienia w tych samych próbkach. Stwierdzono, że precyzyjne oznaczenie zawartości kobaltu na różnych stopniach utlenienia jest możliwe jeśli w próbce nie występuje Co_3O_4 w syntetyzowanych proszkach.

1. Introduction

Thermoelectric power generation as a promising, environment friendly technology of energy conversion has recently attracted the renewed interest for manufacturing thermogenerators as waste heat from automobiles, factories and similar sources offers the significant amount of heat ready for conversion into the electrical energy. The key factor to complete an efficient thermoelectric thermogenerator lies in manufacturing highly effective materials whereas their performance is evaluated by thermoelectric power. CoO_2 -based layered oxides were discovered at the end of XX century as potential compounds for thermoelectric application at high temperature range [1-2]. The further studies by electron, X-ray and neutron diffraction techniques showed a misfit-layered structure of oxides with CoO_2 conducting layers [3-5]. The misfit structure is assumed to be a natural superlattice, in which

two subsystems play totally different roles. The CoO_2 subsystem is responsible for creation large thermoelectric power factor while the disordered rock salt-type subsystem significantly lowers the lattice conductivity [5]. From the charge neutrality, the Co ions are either Co^{3+} or Co^{4+} in the CoO_2 sheets and their nominal ratio in $\gamma\text{-Na}_x\text{CoO}_2$ ($x=0.70$) is $\text{Co}^{3+}:\text{Co}^{4+}=3:7$ while the nominal valence of cobalt is close to $\text{Co}^{+3.23}$ [6] or to +3.5 [7] in $\text{Ca}_3\text{Co}_4\text{O}_9$ compound with the structural formula of $[\text{Ca}_2\text{CoO}_3]_{0.62}\text{CoO}_2$. In the real compound a displacive modulation of the atomic sites occurs through the mutual interaction between both systems and a good electronic conduction takes place. The average valence state of cobalt can be determined by measurement of the oxygen content in the material after reduction in hydrogen atmosphere [8] or by wet-chemical redox analysis [9] but such quantity can not reveal the number of cobalt ions active in the charge transfer. Therefore, only the actual

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concentration of the cobalt ions in the resultant polycrystalline ceramic instead of the average valence state will determine their thermoelectric efficiency.

The paper presents the results of the measurement of cobalt ions concentration at various oxidation state as elaborated for sodium and calcium cobaltite. The results from different measurements were compared and discussed.

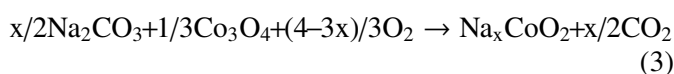
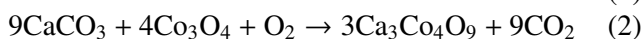
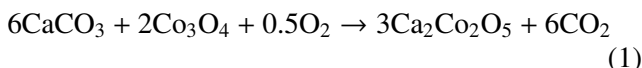
2. Experimental

Sodium and calcium cobaltites were prepared by the solid state reaction. Starting materials for preparation are shown in Table 1. All reagents were of chemical grade purity delivered by Merck. The mixtures of reagents were weighed out according to the following reactions:

TABLE 1

Starting materials for sodium and calcium cobaltite preparation

Kind of synthesis process	Reagents for calcium cobaltites synthesis	Reagents for sodium cobaltite synthesis
solid state reaction	– Co ₃ O ₄ – CaCO ₃ – acetone	– Co ₃ O ₄ – Na ₂ CO ₃ – acetone



Cobalt (II,III) oxide and sodium or calcium carbonates in a molar ratio corresponding to the nominal composition of Na_{0.75}CoO₂, Ca₂Co₂O₅ or Ca₃Co₄O₉ were mixed in an agate mortar for 1 hour with addition of acetone. The batches were then calcined at 800 °C or 850 °C for sodium and calcium cobaltites respectively. The resultant compounds were milled again with acetone for 1 hour in the agate mortar. The powders were then recalcined at 850 °C or 900 °C for sodium and calcium cobaltites respectively. DTA/TG (STA 409 NETZSCH, specimen of 100 mg, heating rate of 10k/min) and XRD studies (EXPERT-Pro Philips, CuK_α monochromatic radiation, λ=1.5406 Å) were applied for characterization of the resultant powders.

Measurement of the total cobalt content and measurement of the cobalt ions fraction at various valence state was performed by the chemical analysis and was developed for the purpose of this paper. The list of chemical reagents (Merck) is shown in Table 2. The procedure consisted of the following steps:

- measurement of the total cobalt content by the two independent spectrophotometric methods with cobalt thiocyanate complexes or cobalt complexes with EDTA
- measurement of Co³⁺ content by spectrophotometric measurement of cobalt complexes with EDTA
- indirect determination of Co⁴⁺ content
- determination of Co²⁺ in free CoO

TABLE 2
Reagents for Co²⁺, Co³⁺ and Co⁴⁺ measurement

Analysis	Reagents
total cobalt content	– 50% solution of NH ₄ SCN – 0,25M solution of EDTA – KIO ₄ – 2M H ₂ SO ₄ – Co standard solution*
Co ²⁺ in CoO	– Franky's reagent (prepared by mixing ethyl acetylacetat in presence of isobutyl alcohol and ethyl ether in the volume ratio 3:20:5) – Co standard solution*
Co ³⁺	– 0,25M solution of EDTA – 2M H ₂ SO ₄ – Co standard solution*
Co ⁴⁺	– 10% KI – HCl conc. – 0,1M sodium thiosulphate – chromium and potassium sulphate solution with concentration of Cr ³⁺ equal to 1mg/ml – 2M H ₂ SO ₄ – Co standard solution*

* Cobalt standard solution with Co²⁺ concentration 1mg/ml (MERCK); working solutions of required concentrations were obtained by diluting of standard solution just before determination

All measurements were performed on the three different cobaltite samples. The procedures are described below:

a) total cobalt content

– Spectrophotometric determination of cobalt thiocyanate complexes

It is assumed that during this process all cobalt from higher oxidation states converts to +2 oxidation state after the reaction with sulphuric acid. 10mg of the cobaltite powder was put into the beaker, then 2ml of water and 2ml of concentrated sulphuric acid were added. The mixture was heated till complete dissolution of the sample. The solution was transferred to the 10ml volumetric flask and fill with water to the mark. 0,5ml of the sample solution were transferred to the 25ml volumetric flask, then 5ml of the NH_4SCN solution and 12,5ml of acetone were added. Absorbance of blue complex solution was measured at λ 620nm against water and the content of cobalt was calculated. Molar absorptivity $\epsilon = 1.91 \cdot 10^4$ [10].

– Spectrophotometric determination of cobalt complexes with EDTA

This determination is based on the complex formation of Co(II) and Co(III) present in cobaltite samples with EDTA and subsequent oxidation of Co(II) complexes to Co(III) complexes with KIO_4 , followed by spectrophotometric determination of the total cobalt content. Obtained results suggest that Co(IV) which could be present in the samples converts to Co(II) in this process.

10mg of the cobaltite powder was put into the beaker, then 10ml of 0,25M EDTA and 0,3ml of 2M H_2SO_4 solutions were added. The mixture was heated till complete dissolution. Next, 0,5g KIO_4 was added for oxidation of cobalt and the samples were heated till complete dissolution of KIO_4 . The solutions were transferred to the 50ml volumetric flasks. Absorbance was measured at λ 534nm against water and cobalt content calculated. Molar absorptivity at λ 534nm $\epsilon=2.94 \cdot 10^2$.

b) measurement of Co^{3+} content

This measurement is based on assumption that only Co(III) forms the stable complexes with EDTA. If the solution is not oxidised than Co(II) ions form only less stable complexes with EDTA and do not influence the absorbance at λ 534nm.

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 $=2.94 \cdot 10^2$.

c) Indirect determination of Co^{4+} content

In the first step the “oxidation factor” was calculated

basing on the assumption that only Co(III) is present in the sample and only 1 electron is involved in reduction of Co^{3+} to Co^{2+} . However, the observed “oxidation factor” was always higher than determined Co(III) amount and usually greater than the total cobalt content. It indicates that the observed excess corresponds to Co(IV) presence. Taking into consideration the fact that reduction of Co(IV) to Co(II) involves 2 electrons instead of 1 electron as in the case of Co^{3+} , then the amount of Co(IV) can be found subtracting the Co(III) content determined according to the procedure described earlier from the value of oxidation factor and dividing the result by two.

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

– Oxidation of Cr^{3+} to $\text{Cr}_2\text{O}_7^{2-}$ by both Co(III) and Co(IV) ions present in cobaltite samples, followed by spectrophotometric determination of dichromate ions content at λ 350nm.

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 the solutions was measured at λ 350nm against water and oxidation factor was calculated. Molar absorptivity $\epsilon = 7,5 \cdot 10^2$ [10].

– Oxidation of I^- to I_2 by both Co(III) and Co(IV) followed by titration with $\text{Na}_2\text{S}_2\text{O}_3$

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.

d) Determination of the content of Co^{2+} only in the form of free CoO

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 described earlier.

3. Results and discussion

XRD studies showed perfect monophasic powders containing only one compound, the relevant cobaltite. DTA/TG study shows stability of the compounds up to 600 °C, below temperature of powder re-calcinations. Small mass losses were observed above 600 °C and they can be attributed to the oxygen loss because of cobalt

reduction. Besides, several endothermic peaks (Fig. 1-2) were found above temperature of specimens calcinations (850 °C for sodium and 900 °C for calcium cobaltite). Those reactions are connected with decomposition of cobaltite, its reduction and oxygen evolution according to the equilibrium diagram [11]. Besides, there is one peak at 914°C in both calcium cobaltite specimen (Fig.

1) and it was not found in sodium cobaltite (Fig.2). That peak could be ascribed to decomposition of free Co_3O_4 to CoO as this transition is reversible and takes place at about 900 °C. It could be assumed that both calcium cobaltite specimens contain free, non-reacted Co_3O_4 , while sodium cobaltite specimen seems to be free of that oxide.

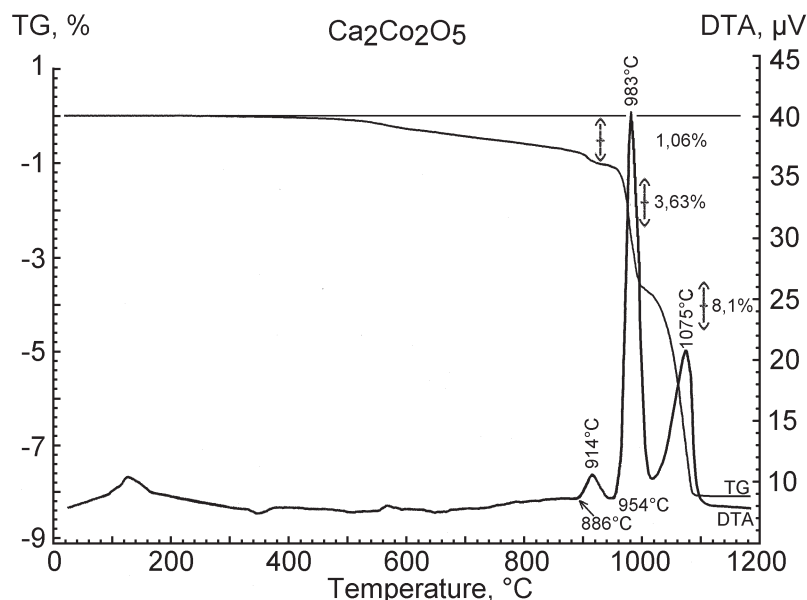


Fig. 1. DTA/TG of the sample with nominal composition of $\text{Ca}_2\text{Co}_2\text{O}_5$ after calcination at 850 °C and recalcination at 900 °C

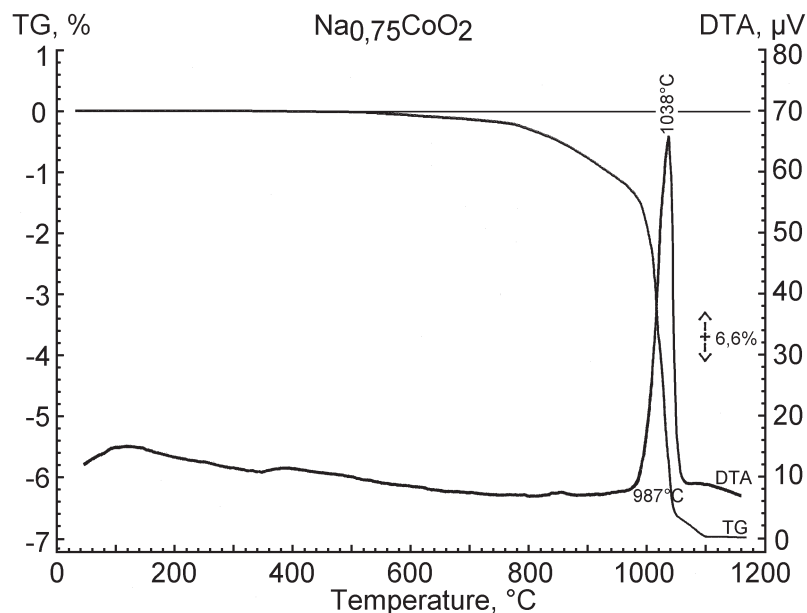


Fig. 2. DTA/TG of the sample with nominal composition of $\text{Na}_{0.75}\text{CoO}_2$ after calcination at 800 °C and recalcination at 850 °C

Both, sodium and calcium cobaltites dissolve easily in EDTA solution. Cobalt (III) forms a red coloured complex of high stability with EDTA in a weak acid solution. pK value given in the literature [10] equals

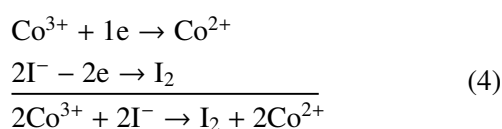
to 40,6. It is the most stable complex which EDTA as a ligand forms with metal ions. Resulting red colour of the solution indicates that Co^{3+} present in materials under investigation forms complex with this ligand, which can

be used for Co^{3+} quantification. Co^{2+} forms less stable complex of much lower sensitivity and do not contribute to the absorbance value at the maximum wavelength of Co^{3+} complex ($\lambda = 534\text{nm}$).

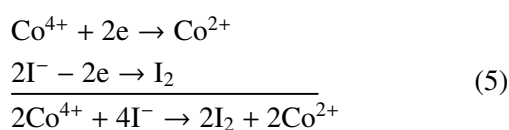
Cobalt (III) and cobalt (IV) can undergo redox reactions. Standard redox potential of $\text{Co}^{3+}/\text{Co}^{2+}$ couple is very high and equals 1.84V [10] what indicates that the reactions with Cr^{3+} and I^- can go towards oxidation to $\text{Cr}_2\text{O}_7^{2-}$ and I_2 respectively ($E^\circ [\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}] = 1.33\text{V}$ [6]; $E^\circ [\text{I}_2/\text{I}^-] = 0.536\text{V}$ [10]).

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 [10]. In materials containing Co(III) and Co(IV) the following reactions can be expected:

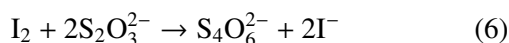
Reactions of Co(III) with I^- :



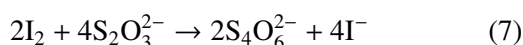
Reactions of Co(IV) with I^- :



Titration reactions:



The mole ratio of $\text{Co}^{3+}/\text{S}_2\text{O}_3^{2-} = 1:1$



The mole ratio of $\text{Co}^{4+}/\text{S}_2\text{O}_3^{2-} = 1:2$

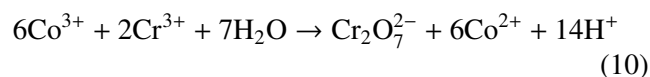
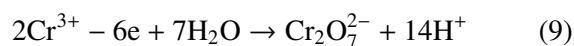
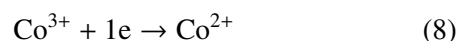
Results obtained from titration analysis cannot differentiate between Co^{3+} and Co^{4+} content. However, they can be used for the determination of the "oxidation factor". In this case the assumption is made that in the sample exists only Co^{3+} which consumes 1 electron per 1 ion. Calculation based on the volume of standard thiosulphate solution used for the determination of reduced iodine in

the redox reaction will give the content of cobalt on higher oxidation states recalculated as Co^{3+} .

In order to assess 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 resultant difference must be divided by 2 (number of consumed electrons by Co^{4+}) and finally it will give the content of Co^{4+} in the examined sample.

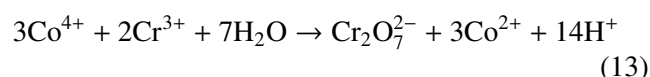
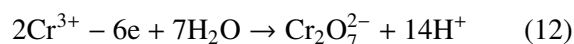
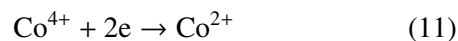
Other possibility was found because the difference in standard redox potential indicates that Co^{3+} and Co^{4+} ions can oxidize Cr^{3+} ions according to the possible reactions:

Reactions of Co^{3+} with Cr^{3+} :



The ratio of $\text{Co}^{3+}/\text{Cr}_2\text{O}_7^{2-} = 6:1$

Reactions of Co^{4+} with Cr^{3+} :



The ratio of $\text{Co}^{3+}/\text{Cr}_2\text{O}_7^{2-} = 3:1$

In Fig.3 absorption spectra of $\text{K}_2\text{Cr}_2\text{O}_7$ (Cr^{6+}) (curve 1) and Cr^{3+} 1mg/ml (curve 2) in UV-Vis range are presented. At $\lambda=350\text{nm}$ 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+} .

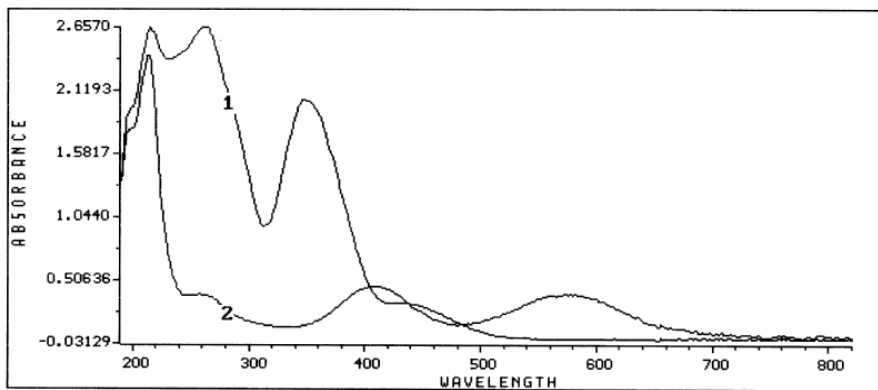


Fig. 3. Curve 1 – absorption spectra of dichromate standard sample; Curve 2 – absorption spectra of Cr³⁺ standard sample

In Fig. 4 the absorption spectra of calcium cobaltite sample after reaction with Cr³⁺ (curve 1), and standard sample of chromium (III) of concentration 1mg/ml (curve 2) are presented. The well shaped Cr₂O₇²⁻ absorption band is

seen. The absorbance value can be applied for the determination of “oxidation factor” recalculated as Co³⁺ content similarly to the aforementioned iodometry.

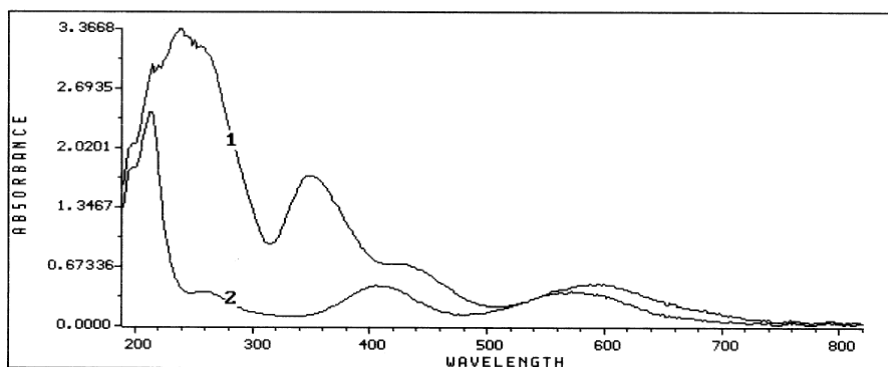
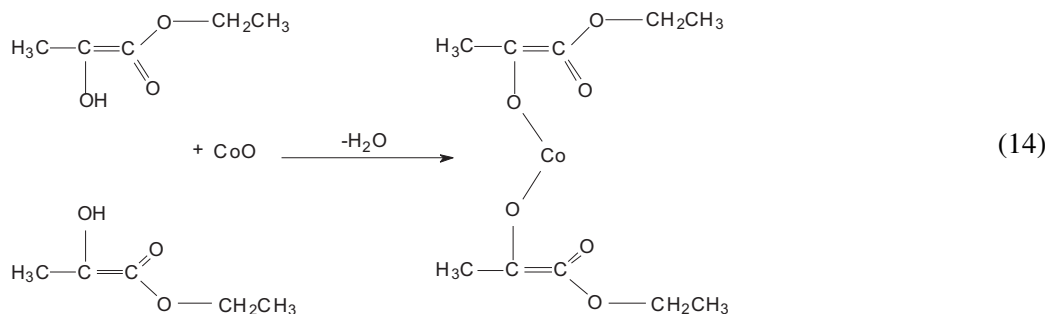


Fig. 4. Curve 1 – absorption spectra of calcium cobaltite sample after reaction with Cr³⁺; Curve 2 – absorption spectra of Cr³⁺ standard sample

Samples of cobaltites can contain free CoO phase for several reasons: nonreacted starting cobalt oxide or precipitation of CoO from the cobaltite structure during cooling. Our investigations revealed that it reacts simi-

larly 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. However, it must be mentioned that the applied procedure with Franky's reagent do not give possibility for measurement of Co(II) if it is present in Co_3O_4 because the latter does not react with Franky's reagent. Results of all analyses are shown in table 3. The values in the 2nd and 3rd column show mass percentage of Co(II) and Co(III) respectively while the values in column 5th and 7th show mass percentage of Co(IV) as measured by two different methods (redox reaction with Cr^{3+} or I^-). The total cobalt content as measured by complexes with SCN and EDTA in shown in columns 8th and 9th respectively. Finally, the 10th column contains calculated

values of the total cobalt content as a result of adding Co(II) , Co(III) and Co(IV) as measured by the reaction with Cr^{3+} or I^- . The latter values are in brackets in column 10th. Comparison of the results of the total cobalt content as measured and summed the separated valence state (columns 8-10) gives accuracy and reliability of the elaborated method. Values presented in Table 3 (8th and 9th columns) show that the total cobalt content determination carried out by two independent methods gives the same reliable results. Small discrepancies result from the measurement errors. Presented results show that the total content of cobalt in all measured samples is lower than the "oxidation factor" determined by two independent redox methods. The existence of the excess value proves occurrence of Co^{4+} form in the as-synthesized materials. The discrepancy between iodometry and chromatometry is in most cases within the measurement error.

TABLE 3

Results of chemical analysis

sample	Co^{2+} in CoO [wt%]	Co^{3+} EDTA [wt%]	oxidatio n factor Cr^{3+}	Co^{4+} Cr [wt%]	oxidatio n factor J	Co^{4+} J [wt%]	Σ Co SCN [wt%]	Σ Co EDTA [wt%]	Σ from columns 2+3+5 (2+3+7)
1	2	3	4	5	6	7	8	9	10
$\text{Na}_{0,75}\text{CoO}_2$	3,4 $\pm 0,3$	41,28 $\pm 0,5$	63,4 $\pm 0,6$	11,1 $\pm 0,6$	66,5 $\pm 0,5$	12,5 $\pm 0,5$	55,3 $\pm 0,6$	56,5 $\pm 0,5$	55,8 (57,0)
$\text{Ca}_2\text{Co}_2\text{O}_5$	–	21,9 $\pm 0,5$	50,2 $\pm 0,6$	14,1 $\pm 0,6$	49,2 $\pm 0,5$	13,8 $\pm 0,5$	42,0 $\pm 0,5$	42,8 $\pm 0,5$	36,0 (35,7)
$\text{Ca}_3\text{Co}_4\text{O}_9$	0,8 $\pm 0,2$	24,6 $\pm 0,5$	56,6 $\pm 0,5$	16 $\pm 0,5$	56,1 $\pm 0,5$	15,7 $\pm 0,5$	43,8 $\pm 0,5$	43,7 $\pm 0,4$	41,4 (41,1)

Total cobalt content calculated by summarising results obtained from independent determination of Co(II) , Co(III) and Co(IV) (10th column) is in a good accordance with value of determined total cobalt amount in the case of sodium cobaltite. In samples of lower calculated value than measured total value the presence of unreacted Co_3O_4 (DTA/TG) can cause the difference. It is assumed that the Co^{2+} present in this oxide phase is not analysed by described procedures as Franky's reagent can react only with free CoO phase. On the other hand, both Co(II) and Co(III) in Co_3O_4 were analysed if the total cobalt content was measured by dissolution of the cobaltite powder and reduction of the all cobalt form to Co(II) . Thus the measured total cobalt content (column 8 or 9) must be always higher than the value in column 10th (summing).

The results of chemical analysis allow calculation of the cobalt valence state in the resultant cobaltite: +3,21 for sodium and +3,39 for both calcium cobaltite. The values are in the range of the reported results measured by wet

chemical redox analysis [9] but they are more precise as precipitated $\text{CoO/Co}_3\text{O}_4$ are excluded from calculation. Application of the elaborated method can be useful in determination of the stability of the crystal lattice with the given cobalt vacancies and cobalt valence state.

4. Conclusions

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 combined method of chemical analysis and DTA/TG are more accurate than XRD in detection of free cobalt oxides (CoO and/or Co_2O_3) non-active in the thermoelectric effect. Moreover, the precise cobalt valence state in the semiconducting cobaltite can be calculated.

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