

# Investigations on the hydrothermal synthesis of pure and Mg-doped nano-CuCrO<sub>2</sub>

Dirk Friedrich<sup>1,\*</sup>, Claudia Wöckel<sup>1</sup>, Sebastian Küsel<sup>2</sup>, Robert Konrath<sup>2</sup>, Harald Krautscheid<sup>2</sup>, Reinhard Denecke<sup>1</sup>, Bernd Abel<sup>1,3</sup>

<sup>1</sup>Wilhelm-Ostwald-Institute of Theoretical and Physical Chemistry, Department of Chemistry and Mineralogy, University of Leipzig, Leipzig, Germany

<sup>2</sup>Institute for Inorganic Chemistry, Department of Chemistry and Mineralogy, University of Leipzig, Leipzig, Germany

<sup>3</sup>Chemical Department, Leibniz Institute of Surface Modification (IOM), Leipzig, Germany

## Email address:

dirkf2283@outlook.de (D. Friedrich), claudia.woeckel@uni-leipzig.de (C. Wöckel), sebastiankuesel@gmx.de (S. Küsel), robert.konrath@gmx.de (R. Konrath), krautscheid@rz.uni-leipzig.de (H. Krautscheid), denecke@uni-leipzig.de (R. Denecke), bernd.abel@uni-leipzig.de (B. Abel)

## To cite this article:

Dirk Friedrich, Claudia Wöckel, Sebastian Küsel, Robert Konrath, Harald Krautscheid, Reinhard Denecke, Bernd Abel. Investigations on the Hydrothermal Synthesis of Pure and Mg-Doped Nano-CuCrO<sub>2</sub>. *American Journal of Nano Research and Application*. Special Issue: Advanced Functional Materials. Vol. 2, No. 6-1, 2014, pp. 53-60. doi: 10.11648/j.nano.s.2014020601.17

**Abstract:** This paper presents some investigations on the hydrothermal synthesis of nano-CuCrO<sub>2</sub>. Several successively altered synthesis protocols are used to investigate effects of changing the mineralizer amount, lowering reaction temperature and addition of a reducing agent. As a result modified protocols for the hydrothermal synthesis of pure and Mg-doped CuCrO<sub>2</sub> are presented. Different washing and annealing steps are used to perform a comparative XRD-study on these materials.

**Keywords:** Delafossite, CuCrO<sub>2</sub>, Hydrothermal Synthesis

## 1. Introduction

The compound CuCrO<sub>2</sub> is a promising material for optoelectronic applications. It belongs to a group of ternary oxides that crystallize in the delafossite structure. The structure exists in two polytypes, which are distinguishable by their stacking order along the c-axis. 3R-CuCrO<sub>2</sub> exhibits a stacking order AaBbCcAaBbCc, 2H-CuCrO<sub>2</sub> a stacking order AaBbAaBb [1]. In both structures there are layers of edge sharing CrO<sub>6</sub>-octahedra (capital letters in stacking order) which are connected by layers of monovalent copper atoms (small letters in stacking order). Each copper atom exhibits a linear coordination towards oxygen atoms of two different CrO<sub>6</sub>-layers. Nanosized CuCrO<sub>2</sub> and Mg-doped CuCrO<sub>2</sub> have been successfully applied in p-type dye sensitized solar cells (DSSCs) [2–5]. Comparison of application of pure and Mg-doped nano-CuCrO<sub>2</sub> in p-type DSSCs revealed an optimal performance for CuCr<sub>0.9</sub>Mg<sub>0.1</sub>O<sub>2</sub> [3]. The optical transmittance of CuCrO<sub>2</sub> based electrodes and the short circuit current density of p-type DSSCs incorporating these electrodes improved upon Mg-doping. This increased current density could be caused by lowering the electrical resistivity upon doping, as it has been reported multiple times [6–10].

However, in this case the decrease in average crystallite size from around 15 nm to 10 nm upon incorporation of Mg has been identified as major improvement. CuCr<sub>0.9</sub>Mg<sub>0.1</sub>O<sub>2</sub> based porous electrodes show a higher surface area than undoped ones. This leads to a higher amount of adsorbed dye and ultimately to higher short circuit densities. Therefore, a small reduction in crystallite size resulted in improvement of DSSC performance. There have been several other reports on the hydrothermal synthesis of CuCrO<sub>2</sub> [11–17]. These reports all differ in a key component to the aforementioned procedures. They all use Cu<sub>2</sub>O as starting material, a compound with monovalent copper, whereas the aforementioned procedures use copper(II) nitrate. For the hydrothermal synthesis of the delafossite material CuGaO<sub>2</sub> similar procedures based on Cu(NO<sub>3</sub>)<sub>2</sub> are published [18, 19]. However, in these reports the necessary reduction of copper is achieved by the addition of alcohols as reducing agent. As reported, hydrothermal synthesis of CuCrO<sub>2</sub> is achieved despite the absence of an apparent reducing agent, a fact that has not been further commented yet. Another aspect that has not been further investigated is the actual dopability of CuCrO<sub>2</sub> with magnesium under the applied hydrothermal conditions. Other reports on CuCr<sub>1-x</sub>Mg<sub>x</sub>O<sub>2</sub> involve high temperature annealing

steps and the maximum reported amount of Mg that is incorporated into the delafossite host structure varies depending on the applied method [9]. In some case the spinel type material MgCr<sub>2</sub>O<sub>4</sub> can already be detected as a by-product via XRD for  $x > 0.02$  [20], thus limiting Mg-doping. In this publication we report on investigations on the hydrothermal synthesis of pure and Mg-doped nano-CuCrO<sub>2</sub>. We present a modified hydrothermal synthesis of pure and Mg-doped CuCrO<sub>2</sub> with the potential to decrease average crystallite size of these materials.

## 2. Experimental

### 2.1. Analytical Measurements

Powder X-ray diffraction data were collected using a STOE STADIP powder diffractometer with Debye-Scherrer geometry. Source of radiation was a sealed tube with Cu-anode ( $\lambda$  (Cu-K $\alpha$ ) = 154.06 pm). The radiation was monochromatized using a Ge-single crystal. All measurements were performed at room temperature using a position sensitive detector. Samples were measured in transmission mode with a flat sample geometry. The powdered samples were spread evenly on a circular polymer with diluted glue ("Elmer's white glue"). When the samples had been dried, they were inserted into sample holders and fixed with a mask of 1 cm inner diameter. These samples were measured in a  $2\theta$ - $\omega$ -coupled mode and continuously rotating around the sample center on an axis perpendicular to the sample surface. Simultaneous thermal analysis was performed using a "STA 449 F1 Jupiter" TG/DTA device (Netzsch) coupled with a "QMS 403 C" electron ionization quadrupole mass spectrometer (Aëolos). The samples were transferred into Al<sub>2</sub>O<sub>3</sub> crucibles, the oven was evacuated and flooded with helium carrier gas before measurements were started. The samples were heated from 40-550 °C with a rate of 15 K/min and isothermally treated at this temperature for 20 min. DTA reference was an empty Al<sub>2</sub>O<sub>3</sub> crucible. REM pictures have been obtained using a "Ultra 55" (Carl Zeiss SMT) and EDX analysis was performed using a "AXS Quantax" (Bruker AXS Microanalysis).

### 2.2. Synthetical Procedures

All reagents were of analytical grade (Sigma-Aldrich) and used without further purification. Starting materials: Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, CuCl<sub>2</sub>·2H<sub>2</sub>O, CrCl<sub>3</sub>·6H<sub>2</sub>O. All hydrothermal reactions have been performed in 20 ml PTFE-lined stainless steel autoclaves. A series of different protocols for the synthesis of CuCrO<sub>2</sub> was tested. For each protocol an amount between 1-3 mmol Cu(NO<sub>3</sub>)<sub>2</sub> is dissolved together with 1-x equivalents of Cr(NO<sub>3</sub>)<sub>3</sub> and x equivalents of Mg(NO<sub>3</sub>)<sub>2</sub>. We tested  $x = 0.05$  and 0.1. The NaOH mineralizer is added to the homogeneous solution under stirring. For an excess of NaOH it is added in the form of pellets. For the addition of equivalent amounts a solution of known concentration (around 2 mol/l) is used. Autoclaves are filled to 50 -70 % of their volume. The closed

vessels are heated to their reaction temperature within 3 h, this temperature is maintained for 60 h and now the vessels are cooled down to ambient temperature within 3 h. The olive to dark green precipitates are collected by centrifugation. Half of the obtained solid products are washed several times with water and *iso*-propanol. The other half is once washed with a 0.1M hydrochloric acid and then washed with a 28 % aqueous ammonia solution till the centrifugate remains colorless. After washing several times with water and *iso*-propanol the final products are dried in air at 100 °C. Differences between the performed protocols are listed in table 1.

**Table 1.** Protocols for the hydrothermal synthesis of CuCrO<sub>2</sub>, EG = ethylene glycol

	Temperature	Distinguishing features
P1	240 °C	excess NaOH
P2	240 °C	5 eq NaOH
P3	200-210 °C	5 eq NaOH
P4	240 °C	a: 5 eq NaOH, Cl <sup>-</sup> instead NO <sub>3</sub> <sup>-</sup> b: 5 eq NaOH , washed Cl-free
P5	200-210 °C	5 eq NaOH, 0.1-0.5 ml EG
P6	200-210 °C	5-x eq NaOH, x eq Mg, 0.1-0.5 ml EG

## 3. Results and Discussion

### 3.1. Hydrothermal Synthesis of CuGaO<sub>2</sub> and CuCrO<sub>2</sub>

As it has been reported, the reduction in the crystallite size of nano-CuCrO<sub>2</sub> by Mg-doping is suggested to be a main advantage for application of this material in p-type DSSCs [3]. A comparison of two reports on the hydrothermal synthesis of CuGaO<sub>2</sub> and nano-CuCrO<sub>2</sub> is depicted in Table 2[2, 18]. Both protocols use a mixture of Cu(II) and Cr(III)-nitrate as starting material. It can be seen, that for the hydrothermal synthesis of CuGaO<sub>2</sub> ethylene glycol is used as reducing agent to form monovalent copper. For the formation of CuCrO<sub>2</sub> no explicit reducing agent is mentioned and the reaction temperature is 50 °C higher. The pH for the synthesis of CuGaO<sub>2</sub> was set to values between 2.6 and 7.5 by addition of mineralizer. With no mineralizer the delafossite phase was only a by-product. Higher crystallinity was achieved by higher pH. According to the authors the optimal amount of mineralizer to be added for lowering the crystallite size is equal to the amount necessary to precipitate Cu(OH)<sub>2</sub> and Ga(OH)<sub>3</sub>. In an attempt to potentially lower the crystallite size of nano-CuCrO<sub>2</sub> we have tried to adapt aspects of hydrothermal synthesis of CuGaO<sub>2</sub> to the synthesis of CuCrO<sub>2</sub>. We have tried out several experimental protocols, all using an equimolar solution of Cu(II) and Cr(III) salts.

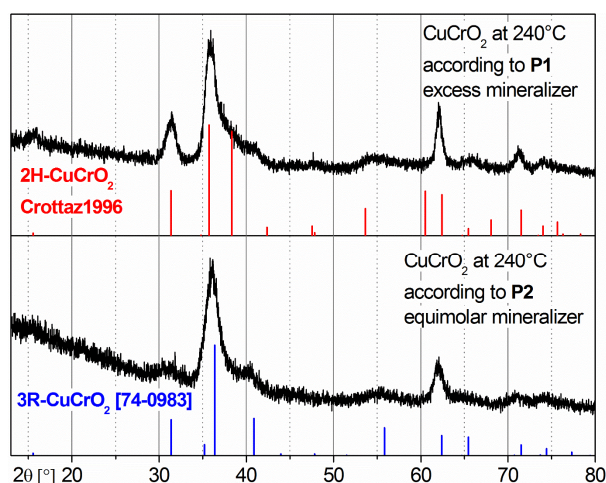
We added exactly 5 equivalents NaOH to precipitate "CuCr(OH)<sub>5</sub>" from a solution of Cu(II) and Cr(III) nitrate in procedure P2. Hydrothermal treatment of this mixture at 240°C for 60 h delivers nanocrystalline 3R-CuCrO<sub>2</sub>. The literature procedure P1, using excess mineralizer delivers a mixture of 2H and 3R-CuCrO<sub>2</sub>. The XRD patterns of both products can be seen in Fig. 1. P1 delivers a product, which shows a little more defined crystallinity as compared to P2, which is indicated by slightly broader reflections in the XRD

pattern of P2. This observation is similar to findings concerning the hydrothermal synthesis of  $\text{CuGaO}_2$ . Hence, a shift from excess mineralizer to an equimolar amount might result in reduction of crystallite size.

**Table 2.** Comparison of literature procedures for hydrothermal synthesis of  $\text{CuGaO}_2$  and  $\text{CuCrO}_2$

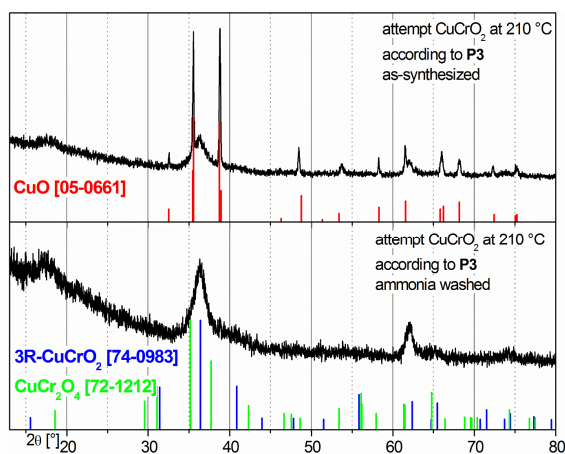
Reference	$\text{CuGaO}_2$ [18]	$\text{CuCrO}_2$ [2]
Starting materials	$\text{Cu}(\text{NO}_3)_2$ , $\text{Ga}(\text{NO}_3)_3$ ,	$\text{Cu}(\text{NO}_3)_2$ , $\text{Cr}(\text{NO}_3)_3$ ,
Reducing agent	Ethylene Glycol	-
Temperature	190 °C	240 °C
Duration	56 h	60 h
Mineralizer	KOH or NaOH	NaOH
pH	2.6-7.5	>12
Washing steps	Subsequent: $\text{NH}_3$ (28 %) $\text{HNO}_3$ (diluted) $\text{H}_2\text{O}$	Sequence: HCl (diluted) EtOH

### 3.2. Using an Equimolar Amount of Mineralizer



**Figure 1.** XRD patterns of hydrothermally synthesized  $\text{CuCrO}_2$ ; top: according P1 with reference phase  $2\text{H-CuCrO}_2$  [1]; bottom: according P2 with reference phase  $3\text{R-CuCrO}_2$  [JPCDS 74-0983]

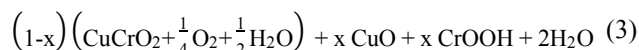
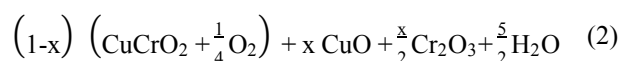
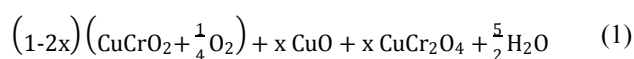
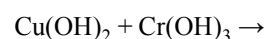
### 3.3. Lowering the Temperature



**Figure 2.** XRD patterns of hydrothermally synthesized  $\text{CuCrO}_2$  (according P3); top: water washed sample and reference  $\text{CuO}$  [JPCDS 05-0661]; bottom: ammonia washed sample and references  $3\text{R-CuCrO}_2$  [JPCDS 74-0983] and  $\text{CuCr}_2\text{O}_4$  [JPCDS 72-1212]

Several groups using  $\text{Cu}_2\text{O}$  as starting material quote that  $\text{CuCrO}_2$  can be obtained in a temperature range between 180 and 250 °C [11–14]. With procedure P3 we attempted to lower the reaction temperature to 200–210 °C. However this protocol produced major amounts of  $\text{CuO}$ , as detected by XRD. When the copper oxide is removed by washing with concentrated ammonia, only a few broad reflections remain in the XRD pattern. XRD data of a products according to P3 is depicted in Fig. 2.

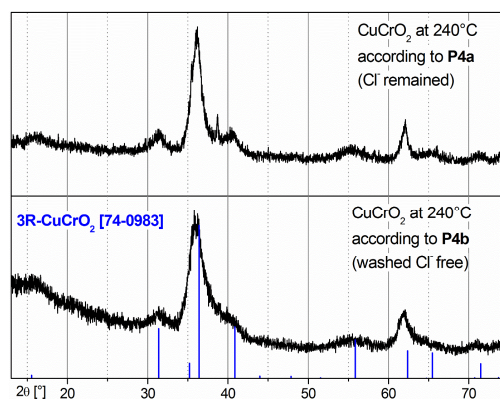
The two most prominent reflections in an ammonia washed sample are very broad and found at  $2\theta$ -values of  $36.4^\circ$  and  $62.1^\circ$ . They do fit the major reflections of nano- $\text{CuCrO}_2$ , the 0 1 2 and 1 1 0 reflection of  $3\text{R-CuCrO}_2$ . Hence, the reaction does work at lower temperatures, but it is not completed within the given time of 60 h. The existence of chromium containing by-products cannot be excluded by the XRD data gathered. Other possible by-products can be amorphous or nano-crystalline. Candidates include  $\text{Cr}_2\text{O}_3$ ,  $\text{CrOOH}$  well as spinel-type  $\text{CuCr}_2\text{O}_4$ . The most prominent XRD-reflections of the latter compound are close to the most intense one of the delafossite phase. At this level of crystallinity they might just be visible by broadening of the  $\text{CuCrO}_2$  reflections. Hence, possible incomplete reactions according to (1), (2) and (3) can be proposed. The ratio of  $\text{CuO}$  to  $\text{CuCrO}_2$  in the as-synthesized products would deliver a hint on the completeness of reaction. Unfortunately it is not feasible to determine reliable results from as-obtained XRD data.  $\text{CuO}$  delivers sharp reflections due to a bigger crystallite size. However, the delafossite phase shows very broad reflections and they could be overlapping with reflections due to  $\text{CuCr}_2\text{O}_4$ . A Rietveld refinement attempting to determine the product to by-product ratio fails. However, lowering the temperature of hydrothermal synthesis conditions does still deliver  $\text{CuCrO}_2$  and could be another possibility of crystallite size reduction.



### 3.4. The Origin of Copper Reduction

We attempted to gather some more insights on the redox mechanism involved in the hydrothermal formation of  $\text{CuCrO}_2$  without additional reducing agent. For that purpose we checked if changing the starting material from nitrates to another anion has an effect. We performed experiments using an equimolar solution of  $\text{CuCl}_2$  and  $\text{CrCl}_3$ . 5 equivalents of  $\text{NaOH}$  were added to precipitate “ $\text{CuCr}(\text{OH})_5$ ”. In case P4b the precipitate has been washed chloride free. According to P4a dissolved  $\text{NaCl}$  remained in the mixture. After hydrothermal treatment at 240 °C nano- $\text{CuCrO}_2$  was obtained in both cases as illustrated by XRD patterns in Fig. 3.





**Figure 3.** XRD patterns of hydrothermally synthesized CuCrO<sub>2</sub>; top: according P4a; bottom: according P4b with reference phase 3R-CuCrO<sub>2</sub> [JPCDS 74-0983]

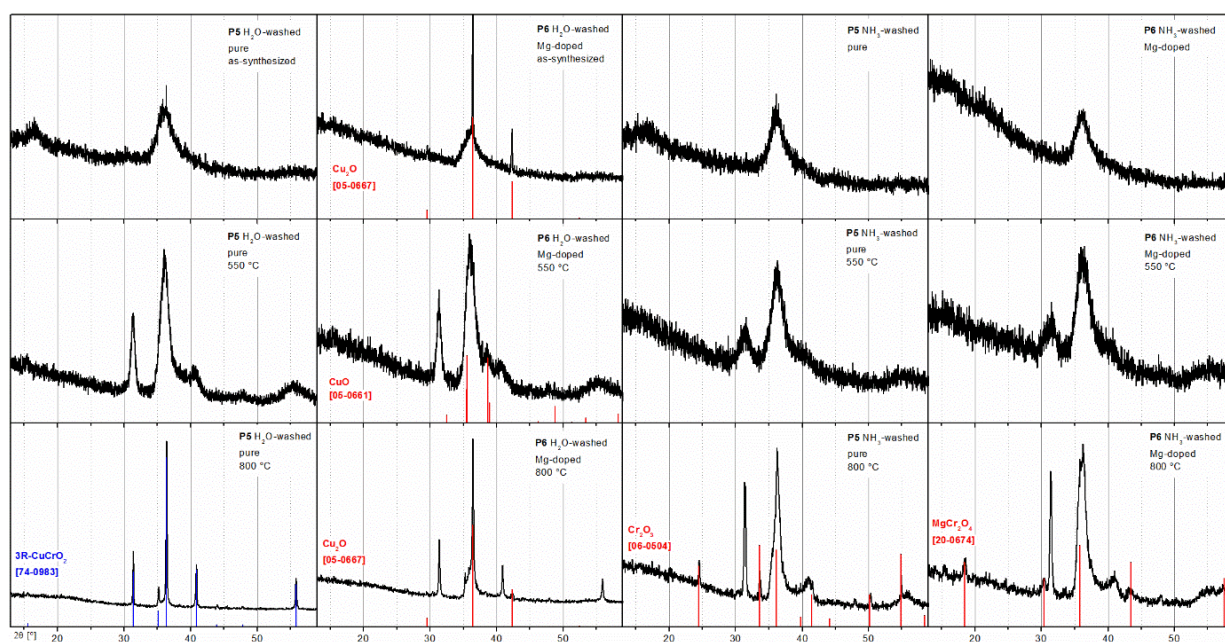
The success of both reactions indicates that reduction of copper into its monovalent state is not promoted by chloride or nitrate. An explanation can be a redox reaction involving chromium, which is supported by literature about the attempted hydrothermal formation of a related delafossite, AgCrO<sub>2</sub>, CrOOH or Cr(OH)<sub>3</sub>, unlike other amphoteric transition metal oxide hydroxides and hydroxides, do not react with Ag<sub>2</sub>O to form AgCrO<sub>2</sub>, but rather these reactions generate a large amount of silver metal. In the presence of Cr(III) which can undergo oxidation into higher valencies, a redox reaction occurs that accelerates the decomposition of Ag<sub>2</sub>O to metallic silver and limits the formation of AgCrO<sub>2</sub> [11]. Recently it has been claimed that chromium is partially oxidized under hydrothermal reaction conditions for the formation of CuCrO<sub>2</sub> [17]. Higher valent chromium could either be incorporated into the delafossite structure, or it can form mixed-valent oxides [21–23].

### 3.5. Protocols with Reducing Agent (P5, P6)

Lowering reaction temperature without the addition of a reducing agent resulted in incomplete reaction. For studying the effect of addition of a reducing agent we further adapted CuGaO<sub>2</sub> reaction conditions by adding ethylene glycol (EG) as a reducing agent to the hydrothermal synthesis of CuCrO<sub>2</sub>. We developed protocol P5 for the hydrothermal synthesis of CuCrO<sub>2</sub> at temperatures between 200–210 °C. A green product showing a few very broad reflections in XRD analysis is obtained. The most prominent reflections could again be matched to 0 1 2 and 1 1 0 reflections of 3R-CuCrO<sub>2</sub>. For CuGaO<sub>2</sub> the ideal EG to water volume ratio is determined to be 0.24. We found that the addition of only 0.1–0.5 ml EG within 10 ml total volume is sufficient. Higher amounts of EG or higher reaction temperature promote the formation of metallic copper. Using this protocol, we attempted the synthesis of doped CuCrO<sub>2</sub> incorporating 5 % of Mg in procedure P6. For that purpose Cr(NO<sub>3</sub>)<sub>3</sub> was partially replaced by Mg(NO<sub>3</sub>)<sub>2</sub> as a starting material. Comparison to P5 shows an immediate difference. The products incorporating magnesium show more prominent Cu<sub>2</sub>O impurities. They can be visually identified after centrifugation as a brick red coloration depicted in Fig. 4.



**Figure 4.** Visual comparison of as-synthesized CuCrO<sub>2</sub> samples; left: Mg-doped according P6; right: undoped according P5; Cu<sub>2</sub>O by-products visible as brick red precipitate



**Figure 5** Comparison of XRD patterns of pure CuCrO<sub>2</sub> samples (according to P5) and 5 % Mg-doped CuCrO<sub>2</sub> (according to P6); left part: water washed samples; right part: ammonia washed samples; top row: as-synthesized; second row: post-TG samples (550 °C); bottom row: annealed samples (800 °C); JPCDS entry number of references given in brackets

A comparative XRD study of pure and Mg-doped CuCrO<sub>2</sub> is shown in Fig. 5. The native products of CuCrO<sub>2</sub> and CuCr<sub>1-x</sub>Mg<sub>x</sub>O<sub>2</sub> as-synthesized by hydrothermal reaction at 200 °C were split into two portions. One portion was only washed with water to preserve all insoluble by-products, the other portion was washed with a 28 % aqueous ammonia solution. The resulting XRD patterns are illustrated in the upper row of Fig. 5. As mentioned, it can be seen, that the H<sub>2</sub>O-washed CuCr<sub>1-x</sub>Mg<sub>x</sub>O<sub>2</sub> contains clearly visible Cu<sub>2</sub>O impurities, whereas this side phase is barely traceable in the

undoped compound. Copper oxide impurities are removed by ammonia wash. The very broad reflections in the first row of XRD patterns indicate a crystallite size in the range of 5 nm for these samples (estimated using the Scherrer equation). Fig. 6 illustrates SEM picture obtained from as-synthesized water and ammonia washed samples obtained according to P5 and P6. The given resolution of these pictures is limited by the device and does barely allow to make out single crystallites. This confirms that crystallite sizes are well below 100 nm.

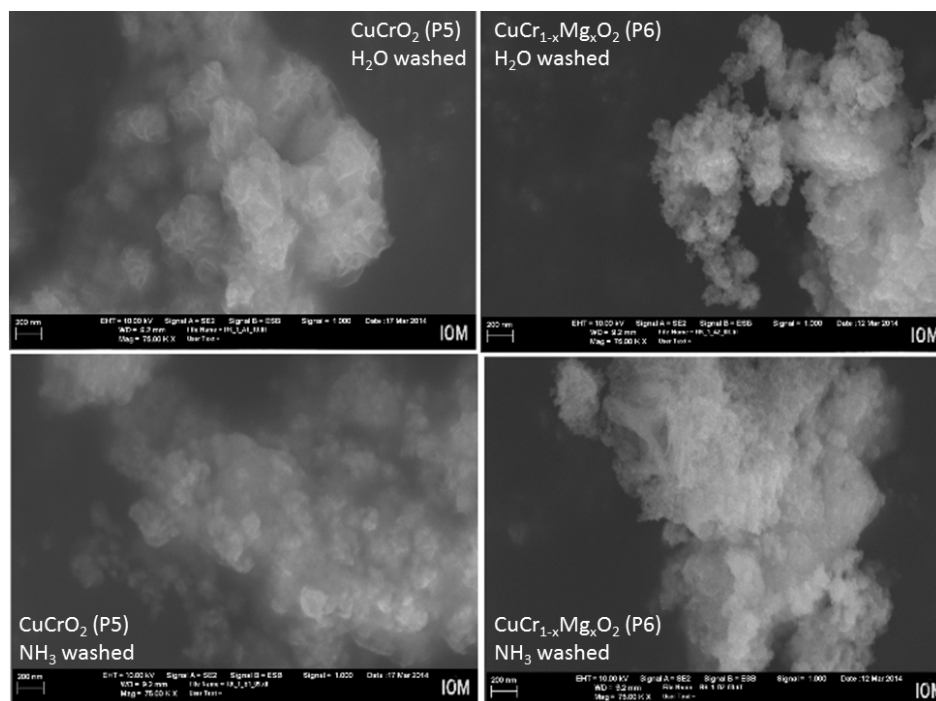


Figure 6 SEM pictures of as-synthesized water and ammonia washed samples according to P5 and P6

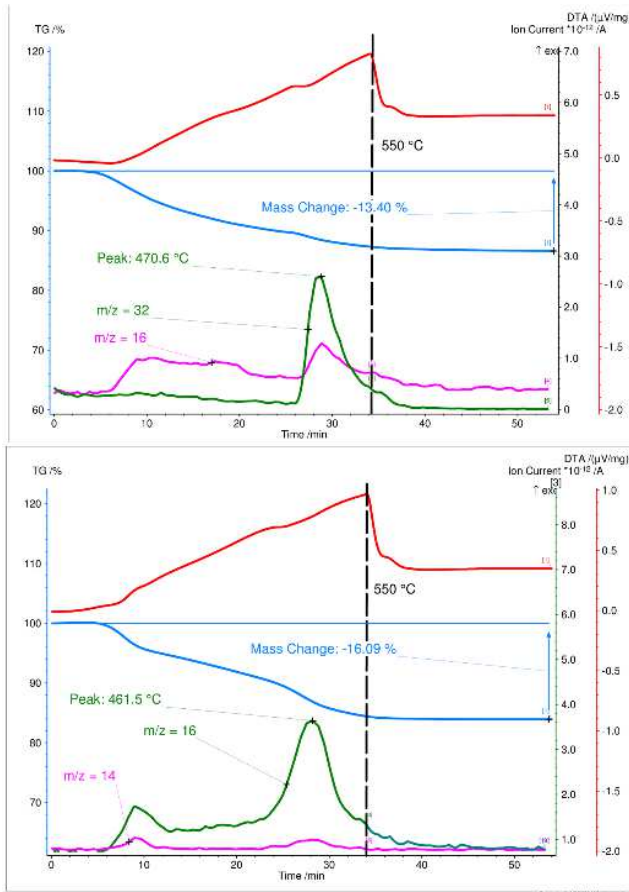
### 3.6. STA Experiments on Nano-CuCrO<sub>2</sub> (P5, P6)

A STA experiment up to 550 °C under He-atmosphere was performed on pure and Mg-doped CuCrO<sub>2</sub>-samples (according to P5 and P6). (STA = simultaneous thermal analysis = TG coupled with QMS). 550 °C is the final temperature of a sintering process used to produce CrCrO<sub>2</sub> based porous electrodes for DSSCs [2]. Fig. 7 illustrates STA results of CuCrO<sub>2</sub> samples obtained via P5.

The STA results of the Mg-doped samples are similar. The TG-graphs show mass losses around 15 % for each of the samples. All of the TG-graphs show overlapped two step mass losses. In the water washed samples the first step between 50 to around 400 °C releases water. This is represented by the m/z trace 16 shown in the graphic (m/z 17 and 18 show parallel peaking, but are not shown here). In a second step between 420 and 550 °C an additional release of O<sub>2</sub> is observed, as indicated by parallel peaking of m/z 16 and 32. The ammonia washed samples do not show release of molecular oxygen. Instead, in the whole region from 60 to 550 °C the mixed release of water and ammonia is observed, as indicated by m/z 14 for ammonia and 16 for water and

ammonia (m/z 15, 17 and 18 show parallel peaking, but are not shown here). The oxygen loss can be caused by a reduction reaction of either divalent to monovalent copper or higher valent to trivalent chromium. Which one it is cannot be distinguished with certainty at this point. The mass loss of around 15 % indicates, that the as-synthesized products have a large surface area that is saturated with chemisorbed water and/or ammonia. The Cu/Cr and Mg/Cr ratio of the post-TG samples were obtained by EDX and are presented in table 3. It can be seen that the water washed products are copper rich, while the ammonia washed ones are copper poor. The Mg/Cr ratio for the doped sample is almost unaltered by the ammonia wash and it fits the ratio as given by the starting materials. XRD patterns of the products of these TG experiments can be seen in the middle row of Fig. 5. The water washed products show increased crystallinity. 3R-CuCrO<sub>2</sub> can be assigned. The diffractograms show anisotropic reflection broadening that can be caused by the formation of hexagonal CuCrO<sub>2</sub> nano-platelets, as already reported for this material and other delafossites [12, 19]. In the pattern of the water washed CuCr<sub>1-x</sub>Mg<sub>x</sub>O<sub>2</sub> traces of Cu-oxide are visible. The ammonia washed samples are

seemingly pure after thermal treatment. The reflections can as well be assigned to 3R-CuCrO<sub>2</sub>. However, they appear much broader than the ones of the water washed samples. A rough estimation using the Scherrer formula delivers a crystallite size in the range of 10 nm for the water washed samples and in the range of 5 nm for the ammonia washed ones. This means that the average crystallite size of CuCrO<sub>2</sub>-based electrodes could potentially be lowered by washing as-synthesized nano-CuCrO<sub>2</sub> with ammonia solution.



**Figure 7.** STA results of a CuCrO<sub>2</sub> sample (according to P5); top: water washed sample; bottom: ammonia washed sample

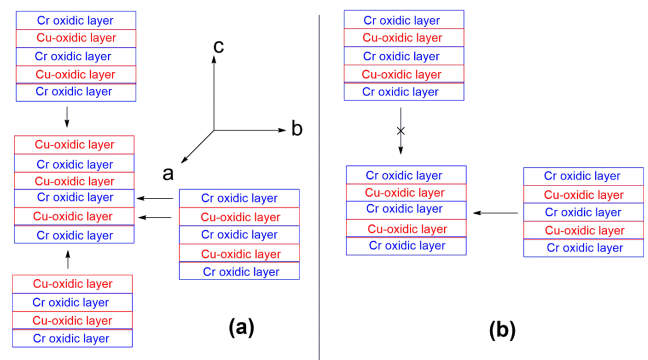
**Table 3.** Atomic Cu/Cr and Mg/Cr ratios of water and ammonia washed post-TG samples (P5, P6)

Protocol: sample	P5: CuCrO <sub>2</sub>	P6: CuCr <sub>0.95</sub> Mg <sub>0.05</sub> O <sub>2</sub>
Cu/Cr {Mg/Cr} H <sub>2</sub> O-wash	1.09	1.12 {0.049}
Cu/Cr {Mg/Cr} NH <sub>3</sub> -wash	0.82	0.77 {0.057}

### 3.2. Annealing Experiments on Nano-CuCrO<sub>2</sub> (P5, P6)

Annealing experiments performed at 800 °C take place in a temperature range which is applicable for solid state reaction to form CuCrO<sub>2</sub>. We performed such annealing steps to crystallize any amorphous by-products that might occur. The according XRD-pattern are shown in the bottom row of Fig. 5. Water washed samples form well crystalline 3R-CuCrO<sub>2</sub> upon annealing. No by-products can be detected for undoped

CuCrO<sub>2</sub>. Mg-doped CuCrO<sub>2</sub> shows traces of copper oxide. No magnesium containing by-products can be detected for doping levels up to 10 %. This indicates, that after annealing at 800 °C Mg should be fully incorporated into the delafossite host structure. Charge neutralization upon Mg-doping of CuCrO<sub>2</sub> demands that either Cu(I) or Cr(III) have to be formally oxidized into higher oxidation states, or oxygen vacancies have to form. Under the following assumptions: 1. Incorporation of 10 % Mg; 2. All chromium remains in its trivalent oxidation state; 3. One equivalent of Copper in the host structure; 4. No oxygen vacancies; one would obtain the following molecular formula: Cu<sup>I</sup><sub>0.9</sub>Cu<sup>II</sup><sub>0.1</sub>Cr<sub>0.9</sub>Mg<sub>0.1</sub>O<sub>2</sub>. However, the copper oxide traces demand that either assumption 2, 3 or 4 is not correct. It has been reported for the delafossite CuRhO<sub>2</sub>, that the incorporation of 10 % of Mg into the host structure causes a Cu(II)/Cu(I) ratio of 0.4 [24]. Transferred to CuCrO<sub>2</sub> that would deliver the following molecular formula: Cu<sup>I</sup><sub>0.61</sub>Cu<sup>II</sup><sub>0.245</sub>Cr<sub>0.9</sub>Mg<sub>0.1</sub>O<sub>2</sub>, which means that 14.5 % of copper used in the starting material would be detected as copper oxide. Another possible explanation for copper oxide impurities would be the incorporation of higher valent chromium into the delafossite host structure, as it has been suggested [17]. However, this should also be the case for undoped CuCrO<sub>2</sub>. Hence, one would expect trace amounts of Cu oxide in that case too. We could not detect such impurities for the water washed sample of CuCrO<sub>2</sub> treated at 800 °C. This does not mean, that no trace amounts of higher valent chromium are present, but it is safe to say, that the incorporation of Mg has a stronger effect. Ammonia washed samples annealed at 800 °C show by-products in their XRD patterns. Cr<sub>2</sub>O<sub>3</sub> can be detected for undoped CuCrO<sub>2</sub> and the spinel compound MgCr<sub>2</sub>O<sub>4</sub> for Mg-doped samples. The XRD patterns that belong to the main 3R-CuCrO<sub>2</sub> phase exhibit anisotropic broadening of reflections. This can be explained by the assumption, that the ammonia washing step not only removes copper oxide impurities, but surface copper oxide layers from delafossite crystallites as well.



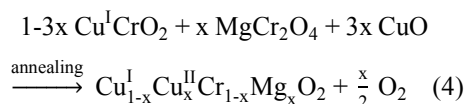
**Figure 8.** Schematic visualization of proposed growth mechanism of CuCrO<sub>2</sub>-nanocrystallites; a: isotropic growth in water washed samples; b: inhibited growth along the c-axis after removal of Cu-oxidic surface layers after ammonia wash

Fig. 8 illustrates how this effect could inhibit the crystallite growth along the c-axis and lead to platelet crystallites, which would cause the observed anisotropic reflection broadening.

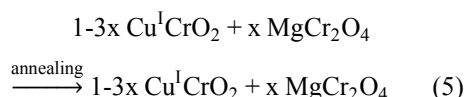


The observed by-products can be explained in several ways. If hydrothermal reaction of pure  $\text{CuCrO}_2$  does not proceed quantitatively, traces of copper oxide and amorphous chromium oxides are left in a product mixture. These by-products react to form  $\text{CuCrO}_2$  during annealing at 800 °C. However, if copper oxide and surface copper oxides are removed by ammonia wash, the leftover chromium oxides appear as  $\text{Cr}_2\text{O}_3$  upon annealing. For the Mg-doped  $\text{CuCrO}_2$  the case is more complicated. In this case, if hydrothermal reaction does not quantitatively produce  $\text{CuCr}_{1-x}\text{Mg}_x\text{O}_2$ , the question is: Does Mg-doping under these conditions work at all?  $\text{MgCr}_2\text{O}_4$  could quantitatively form under hydrothermal conditions instead of magnesium being incorporated in the delafossite host structure. Equation (4) and (5) deliver a possible explanation why  $\text{MgCr}_2\text{O}_4$  is observed only in ammonia washed annealed samples, but not in water washed ones.

After water wash:



After ammonia wash:



The spinel compound could possibly form much faster than delafossite, since there is no redox reaction involved. Hydrothermally formed  $\text{MgCr}_2\text{O}_4$  might not be detectable as by-product in the as-synthesized product as well as the ones heated up to 550 °C due to broad XRD reflections. When annealed at 800 °C it would react with copper oxide to form  $\text{CuCr}_{1-x}\text{Mg}_x\text{O}_2$ , according to (4), and show up as  $\text{MgCr}_2\text{O}_4$ , according to (5). Another explanation of this observation can be the removal of surface copper-oxide layers during the ammonia wash. Since the surface area of such nanocrystals is very high, a relative high amount of surface copper can be removed from the delafossite crystals. This means that the Cu/Cr ratio is decreased within these washed crystallites, as shown in table 3. When these copper deficient crystallites grow upon annealing, they excrete the surplus of chromium in the form of  $\text{Cr}_2\text{O}_3$  for pure  $\text{CuCrO}_2$  and in the form of  $\text{MgCr}_2\text{O}_4$  for Mg-doped  $\text{CuCrO}_2$ . This excretion is therefore necessary to restore a maintainable elemental composition of the delafossite phase. The same effect can cause the appearance of  $\text{Cr}_2\text{O}_3$  in pure  $\text{CuCrO}_2$  samples after ammonia wash and annealing. The true cause might be a combination of incomplete hydrothermal reaction and this annealing effect due to the removal of surface copper oxide.

## 4. Conclusions

We have investigated several protocols for the hydrothermal synthesis of  $\text{CuCrO}_2$ . Our investigations have shown, that using an equimolar amount of NaOH mineralizer

to precipitate " $\text{CuCr}(\text{OH})_5$ " (P2) instead of using excess NaOH (P1) influences crystallinity of the obtained products. A slight XRD signal broadening, indicating a smaller crystallite size is observed for  $\text{CuCrO}_2$  prepared according to P2. A lowering of the reaction temperature from 240 °C to 200-210 °C causes an incomplete reaction within the same reaction time. This results in major amounts of copper oxide detectable by PXRD. We have also shown that an exchange of anions from nitrates to chlorides (P4a) or only hydroxides (P4b) also produces  $\text{CuCrO}_2$ . All the protocols P1-P4 lead to a reduction from divalent to monovalent copper without the explicit addition of a reducing agent. This leads to the conclusion that a partial oxidation of chromium should occur. The exact nature of this redox mechanism still needs further investigation. We have formulated protocols P5 and P6 for the hydrothermal synthesis of pure and Mg-doped  $\text{CuCrO}_2$  involving the addition of ethylene glycol as reducing agent. This enabled a lowering of reaction temperature to 200 °C. A comparative study of products of P5 and P6 has shown that an increase in copper oxide by-product is observed upon Mg-doping, which can be removed by washing steps involving an aqueous ammonia solution. This washing step has an influence on the crystallite size when products are administered to a sintering process up to 550 °C, which is applicable for the formation of  $\text{CuCrO}_2$  based photoelectrodes. The ammonia washing steps can potentially decrease crystallite size in comparison to the annealing of water washed products. Ammonia washed samples annealed at 800 °C exhibit anisotropic reflection broadening and the appearance of  $\text{Cr}_2\text{O}_3$  or  $\text{MgCr}_2\text{O}_4$  by-products in XRD pattern. Both are explainable by the removal of copper oxide by-products and surface copper oxide from the as-synthesized products by ammonia wash. Our modified protocols P5 and P6 can potentially be used to produce  $\text{CuCrO}_2$  based photoelectrodes featuring high surface areas. We are currently exploring their application potential for the manufacturing of  $\text{CuCrO}_2$ -based DSSCs.

## Acknowledgements

For the preparation of SEM and EDX analysis we are thankful to Andrea Prager from the Leibniz Institute of Surface Modification (IOM). Financial support by ESF is gratefully acknowledged. Funded by the European Union and the Free State of Saxony.

## References

- [1] O. Crottaz, F. Kubel, "Crystal structure of copper(I) chromium(III) oxide,  $2\text{H-CuCrO}_2$ " Z. Kristallogr. 211 (1996) 481.
- [2] D. Xiong, Z. Xu, X. Zeng, W. Zhang, W. Chen, X. Xu, M. Wang, Y.-B. Cheng, "Hydrothermal synthesis of ultrasmall  $\text{CuCrO}_2$  nanocrystal alternatives to NiO nanoparticles in efficient p-type dye-sensitized solar cells" J. Mater. Chem. 22 (2012) 24760.

- [3] D. Xiong, W. Zhang, X. Zeng, Z. Xu, W. Chen, J. Cui, M. Wang, L. Sun, Y.-B. Cheng, "Enhanced Performance of p-Type Dye-Sensitized Solar Cells Based on Ultrasmall Mg-Doped CuCrO<sub>2</sub> Nanocrystals" *ChemSusChem* 6 (2013) 1432–1437.
- [4] X. Xu, B. Zhang, J. Cui, D. Xiong, Y. Shen, W. Chen, L. Sun, Y. Cheng, M. Wang, "Efficient p-type dye-sensitized solar cells based on disulfide/thiolate electrolytes" *Nanoscale* 5 (2013) 7963–7969.
- [5] S. Powar, D. Xiong, T. Daeneke, M.T. Ma, A. Gupta, G. Lee, S. Makuta, Y. Tachibana, W. Chen, L. Spiccia, Y.-B. Cheng, G. Götz, P. Bäuerle, U. Bach, "Improved Photovoltages for p-Type Dye-Sensitized Solar Cells Using CuCrO<sub>2</sub> Nanoparticles" *J. Phys. Chem. C* 118 (2014) 16375–16379.
- [6] R. Nagarajan, A.D. Draeseke, A.W. Sleight, J. Tate, "p-type conductivity in CuCr<sub>1-x</sub>Mg<sub>x</sub>O<sub>2</sub> films and powders" *J. Appl. Phys.* 89 (2001) 8022.
- [7] K. Hayashi, K.-i. Sato, T. Nozaki, T. Kajitani, "Effect of Doping on Thermoelectric Properties of Delafossite-Type Oxide CuCrO<sub>2</sub>" *Jpn. J. Appl. Phys.* 47 (2008) 59–63.
- [8] R. Bywalez, S. Götzendörfer, P. Löbmann, "Structural and physical effects of Mg-doping on p-type CuCrO<sub>2</sub> and CuAl<sub>0.5</sub>Cr<sub>0.5</sub>O<sub>2</sub> thin films" *J. Mater. Chem.* 20 (2010) 6562.
- [9] Q. Meng, S. Lu, S. Lu, Y. Xiang, "Preparation of p-type CuCr<sub>1-x</sub>Mg<sub>x</sub>O<sub>2</sub> bulk with improved thermoelectric properties by sol-gel method" *J. Sol-Gel Sci. Technol.* 63 (2012) 1–7.
- [10] M.J. Han, Z.H. Duan, J.Z. Zhang, S. Zhang, Y.W. Li, Z.G. Hu, J.H. Chu, "Electronic transition and electrical transport properties of delafossite CuCr<sub>1-x</sub>Mg<sub>x</sub>O<sub>2</sub> (0 ≤ x ≤ 12%) films prepared by the sol-gel method: A composition dependence study" *J. Appl. Phys.* 114 (2013) 163526.
- [11] W.C. Sheets, E. Mugnier, A. Barnabé, T.J. Marks, K.R. Poeppelmeier, "Hydrothermal Synthesis of Delafossite-Type Oxides" *Chem. Mater.* 18 (2006) 7–20.
- [12] S. Zhou, X. Fang, Z. Deng, D. Li, W. Dong, R. Tao, G. Meng, T. Wang, X. Zhu, "Hydrothermal synthesis and characterization of CuCrO<sub>2</sub> laminar nanocrystals" *J. Cryst. Growth* 310 (2008) 5375–5379.
- [13] S. Zhou, X. Fang, Z. Deng, D. Li, W. Dong, R. Tao, G. Meng, T. Wang, "Room temperature ozone sensing properties of p-type CuCrO<sub>2</sub> nanocrystals" *Sensor Actuat. B-Chem.* 143 (2009) 119–123.
- [14] M. Miclau, D. Ursu, S. Kumar, I. Grozescu, "Hexagonal polytype of CuCrO<sub>2</sub> nanocrystals obtained by hydrothermal method" *J. Nanopart. Res.* 14 (2012).
- [15] D. Ursu, M. Miclau, I. Grozescu, "In situ variable temperature X-ray diffraction studies on size scale of CuCrO<sub>2</sub> polytypes with delafossite structure" *J. Optoelectron. Adv. M.* 15 (2013) 768–773.
- [16] D.H. Ursu, M. Miclău, R. Bănică, I. Grozescu, "Hydrothermal synthesis and optical characterization of Ni-doped CuCrO<sub>2</sub> nanocrystals" *Phys. Scr.* T157 (2013) 14053.
- [17] D. Ursu, M. Miclau, "Thermal stability of nanocrystalline 3R-CuCrO<sub>2</sub>" *J. Nanopart. Res.* 16 (2014).
- [18] R. Srinivasan, B. Chavillon, C. Doussier-Brochard, L. Cario, M. Paris, E. Gautron, P. Deniard, F. Odobel, S. Jobic, "Tuning the size and color of the p-type wide band gap delafossite semiconductor CuGaO<sub>2</sub> with ethylene glycol assisted hydrothermal synthesis" *J. Mater. Chem.* 18 (2008) 5647.
- [19] M. Yu, T.I. Draskovic, Y. Wu, "Understanding the Crystallization Mechanism of Delafossite CuGaO<sub>2</sub> for Controlled Hydrothermal Synthesis of Nanoparticles and Nanoplates" *Inorg. Chem.* 53 (2014) 5845–5851.
- [20] A. Maignan, C. Martin, R. Frésard, V. Eyert, E. Guilmeau, S. Hébert, M. Poienar, D. Pelloquin, "On the strong impact of doping in the triangular antiferromagnet CuCrO<sub>2</sub>" *Solid State Commun.* 149 (2009) 962–967.
- [21] M.A. Khillia, Z.M. Hanafi, A.K. Mohamed, "Physico-chemical properties of chromium trioxide and its suboxides" *Thermochim. Acta* 59 (1982) 139–147.
- [22] P.G. Harrison, N.C. Lloyd, W. Daniell, "The Nature of the Chromium Species Formed during the Thermal Activation of Chromium-Promoted Tin(IV) Oxide Catalysts: An EPR and XPS Study" *J. Phys. Chem. B* 102 (1998) 10672–10679.
- [23] S. Labus, A. Malecki, R. Gajerski, "Investigation of thermal decomposition of CrO<sub>x</sub> (x ≥ 2.4)" *J. Therm. Anal. Calorim.* 74 (2003) 13–20.
- [24] T.K. Le, D. Flahaut, H. Martinez, N. Andreu, D. Gonbeau, E. Pachoud, D. Pelloquin, A. Maignan, "The electronic structure of the CuRh<sub>1-x</sub>Mg<sub>x</sub>O<sub>2</sub> thermoelectric materials: An X-ray photoelectronspectroscopy study" *J. Solid State Chem.* 184 (2011) 2387–2392.