Chromium containing zinc oxide materials from organobimetallic precursors†

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Zinc oxide has become one of the most important semiconductor materials and it possesses a multitude of properties and applications. An even wider spectrum of properties can be envisioned if an additional element is introduced. On the cation side there is large interest in the combination of ZnO with paramagnetic metal centres like Cr^{III}. Two new single source precursors containing "ZnO" and chromium in the ratios 1 : 1 and 1 : 2 are presented. Advantages and disadvantages of using these precursors are reported. One of the advantages is that the geometric organization of the magnetic centres in the ZnO matrix can be preorganized on the molecular scale.

Introduction

Classical solid-state chemistry has provided a variety of inorganic materials possessing enormous importance. An end of this development is not to be foreseen, but it has been argued that rational synthesis planning is difficult to realize in solid-state chemistry.[1] To overcome the limitations in mass transport, application of high temperatures is required, at which products are determined by their thermodynamic stability. It is thus difficult to control particle growth and, hence, to obtain refined materials morphologies, such as solids with nanoscale dimensions. The synergistic combination of molecular chemistry and solid-state chemistry solves many of the problems associated with restricted mass transport and, thus, has been named "soft-chemistry". The best-known soft-chemistry process is the sol–gel technique,[2] which is useful for the preparation of binary metal oxides as a result of hydrolysis and polycondensation of metal alkoxide precursors.[3] In comparison, less attention has been devoted to organometallic compounds as precursors for inorganic materials although interesting work can be found in the area of MOCVD.[4] Our group has been using alkylzinc alkoxides containing a central "Zn_4O_4" core as precursors for the preparation of a large variety of ZnO materials.[5-7] The controlled synthesis of bimetallic metal oxides $M^1_xM^2_yO_z$ *via* soft-chemistry is much more demanding, since the reactivity of two precursors might differ significantly. This may result in two separate material-formation steps and thus impede the formation of a single homogeneous phase. It has been shown recently that non-aqueous sol–gel routes are promising regarding the synthesis of bimetallic oxides using precursors, for example, benzyl alcoholates which react with the metal oxides by thermal elimination.[8] In addition, so-called single-source precursors, which contain all required elements in the correct ratio in one molecular compound, have attracted much interest.[9] During the last few years, a considerable number of bimetallic single-source precursors of the metal alkoxide type have been reported,[10] but examples for organobimetallic precursors are rare.[11]

An example for how new properties and applications emerge due to the introduction of a second metal to a functional metal oxide is the following: while zinc oxide represents – already in its pure form – a multifunctional, diamagnetic semiconductor material,[12] ZnO containing paramagnetic transition metal centres (Mn^{2+}, Cr^{3+}, *etc.*) has become increasingly important lately due to its interesting magnetic properties and application in spintronics.[13] In addition to room temperature ferromagnetism in $Zn_{1-x}Cr_xO$ materials, recently reported in two papers,[14] chromium-containing ZnO materials offer additional interesting properties and applications. It has been recognized already in 1928 that $Zn_{1-x}Cr_xO$ materials are active catalysts for the conversion of synthesis gas to methanol and hydrocarbons.[14]

Applications in the fields of varistors or gas-sensors have also been reported.[16,17] The number of synthetic methods known for the preparation of $Zn_{1-x}Cr_xO$ is currently rather limited.[16,18] Much of the attention has focused on classical solid-state routes, which are associated with all the disadvantages mentioned above. Therefore, $Zn_xCr_yO_z$ materials represent an interesting case study for the application of soft-chemistry routes. In the current paper we present a new approach for the preparation of $Zn_xCr_yO_z$ materials using special organobimetallic precursors containing both zinc and chromium in one molecule.

As a starting point, we have selected the above mentioned ZnO precursors containing a "Zn_4O_4" heterocubane core. As demonstrated in Scheme 1, a bimetallic precursor can be obtained either *via* exchange of zinc atoms in the core,[15] by exchange of the methyl group attached to the zinc by a metal-containing fragment, or finally by attaching a metal-containing fragment to the alkoxy group. While we have already reported that the first two possibilities are suitable for the preparation of ZnO materials containing Mn [11] or Ni,[15] we are presenting here the third approach, which leads to precursors for $Zn_xCr_yO_z$ materials. However, it should be noted that heterobimetallic "Zn_4O_4" have also been reported by others: Mo, Fe, Co, Mn,[19] B,[20] Ge,[21] and Si.[22]

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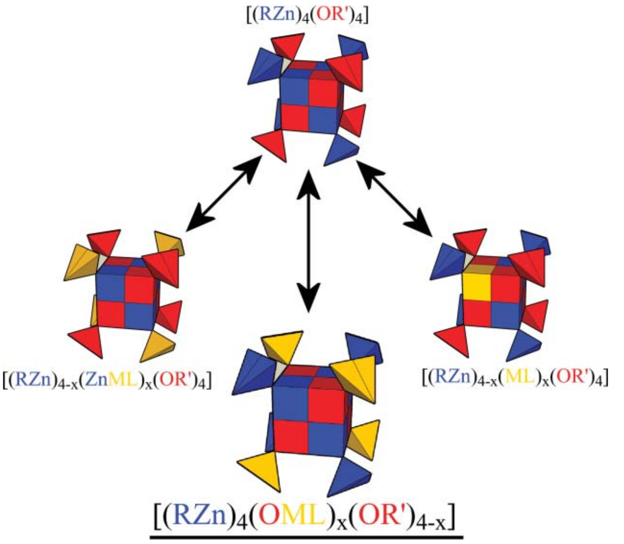
† Electronic supplementary information (ESI) available: SI-1; further analytical data for compound (**4**). SI-2; TGA data. SI-3; PXRD of the product of the thermal oxidation of (**4**). SI-4; photographic images of chromium doped ZnO materials. SI-5; illustration of the effect of chromium on the band gap. See DOI: 10.1039/b916253b



Scheme 1 Three possibilities for obtaining bimetallic precursors containing a heterocubane "Zn_4O_4" core. The metal-containing fragment (M ≠ Zn; yellow colour) can be introduced either (i) *via* the exchange of one zinc atom (indicated by a blue cube) in the core,[15] (ii) by exchange of the methyl ligand attached to the zinc atom (blue tetrahedra),[11] or (iii) by attachment to the alkoxy functionality (red tetrahedra). The latter approach is presented here for the first time.

Experimental

All reactions were carried out under dry nitrogen using standard Schlenk techniques. Chemicals were purchased from Sigma Aldrich and STREM and used after careful purification and drying if necessary. Solvents were dried using standard techniques.

A. Synthesis

$[(BnOH)Cr(CO)_3]$ (**3**)[23] and $[(HOCH(PhCr(CO)_3)_2]$ (**5**)[24] were prepared following procedures reported in the literature.

Preparation of $[MeZnOCH_2Ph]_4$ (2). 20 ml (41 mmol) $ZnMe_2$ 2.05 M in toluene and 40 ml toluene were placed in a Schlenk flask and cooled to −78 °C. 3.9 ml (37 mmol) of anhydrous benzyl alcohol was added dropwise. The reaction mixture was stirred for 1.5 h while warming up to RT. The solvent was removed *in vacuo* and the product was obtained as a white solid. Yield: 6.8 g (98%). Crystallization from toluene–pentane (1 : 1) yielded X-ray quality, block-shaped crystals. ^{1}H-NMR, 250 MHz, $CDCl_3$: $\delta = 6.97$ (m, 5 H, C_6H_5); 4.42 (s, 2 H, $OCH_2C_6H_5$); −0.83 (s, 3 H, $ZnCH_3$). Alternative phenyl containing "Zn_4O_4" heterocubanes are also known from the literature.[25]

Preparation of $[MeZnOCH_2PhCr(CO)_3]_4$ (4). 0.96 g (3.93 mmol) of (benzylalcohol)chromium(0)tricarbonyl (**3**) was dissolved in 140 ml of toluene. After cooling to −78 °C 2.1 ml (4.32 mmol) of $ZnMe_2$ 2.05 M in toluene was added at once. The solution was allowed to warm up to RT and stirred for 1 h, during which it turned into a yellow suspension. Removal of the solvent in vacuum yielded (**6**) as a bright yellow powder (1.24 g, 98%). Crystallization from hot toluene resulted in X-ray quality, needle-shaped crystals. ^{1}H-NMR, 400 MHz, $CDCl_3$: $\delta = 5.25$ (m, 5 H, C_6H_5); 4.26 (s, 2 H, $OCH_2C_6H_5$); −0.71 (s, 3 H, $ZnCH_3$). ^{13}C-NMR, 60 MHz, $CDCl_3$: $\delta = 231.4$ (s, $Cr(CO)_3$); 106.6 (s, *ipso* C_6H_5); 93.4 (s, *ortho* C_6H_5); 92.0 (s, *meta* C_6H_5); 91.7 (s, *para* C_6H_5); 69.5 (s, $C_6H_5CH_2OH$).

Preparation of $[MeZnOCH(PhCr(CO)_3)_2]_2$ (6). 0.736 g (1.61 mmol) of (**5**) was dissolved in 40 ml of toluene. After cooling to −60 °C 1.3 ml (2.47 mmol) of $ZnMe_2$ 1.90 M in toluene was added at once. The solution was allowed to warm up to RT and stirred for 1 h, during which it turned into a yellow suspension. Removal of the solvent in vacuum yielded (**6**) as a bright yellow powder (0.847 g, 98%). Crystallization from hot toluene resulted in X-ray quality, block-shaped crystals.

Preparation of $[MeZnOEtOMe]_4$ (7). 145 ml (275.5 mmol) $ZnMe_2$ 1.9 M in toluene was cooled to −50 °C and 19.45 g (248 mmol) of 2-methoxyethanol was added dropwise under intense stirring. After the addition the solution was allowed to warm up to RT and stirring was continued for 2 h. The solvent was removed *in vacuo* and the product obtained as a colorless, viscous liquid. Yield: 37.3 g (97%). ^{1}H-NMR, 250 MHz, $CDCl_3$: $\delta = 3.84$ (t, 2 H, $ZnOCH_2$); 3.48 (t, 2 H, $ZnOCH_2CH_2$); 3.36 (s, 3 H, OCH_3); −0.76 (s, 3 H, $ZnCH_3$)

Preparation of Cr : ZnO-materials. A stock solution of $[MeZnOCH_2PhCr(CO)_3]_4$ (**4**) in $[MeZnOEtOMe]_4$ (**7**) containing 0.5 mol% of Cr was prepared by dissolving 21.3 mg (16.5 µmol) of (**4**) in 2.04 g (3.27 mmol) of (**7**). Solutions containing 0.05, 0.1 and 0.25 mol% of chromium, respectively, were prepared by diluting the stock solution with additional (**7**).

Oxide materials were prepared by dropping about 0.25 ml of the precursor solution on a ceramic plate, followed by calcination at the desired temperature in air for 20 h.

Preparation Cr : ZnO thin films. To prepare spincoated films of Cr : ZnO on glass, the stock-solution containing 0.5 mol% Cr was diluted with THF in a 1 : 1 ratio. Per film, 0.25 ml of this solution were used for spincoating on plain glass substrates, rotating at 1800 rpm. The obtained films were then calcined in air at 350 °C for 3 h.

B. Characterization

Thermogravimetric analysis was performed on a Netzsch STA 429, powder diffractograms were recorded on a Bruker AXS D8 Advance. A Stoe IPDS diffractometer was used for crystal structure analysis, structure refinement was carried out using ShellX. IR spectra were recorded on a Perkin Elmer Spectrum 100 equipped with an ATR-unit; UV/VIS data was collected on a Cary 100Scan in reflectance mode using an Ulbricht sphere. NMR spectra were recorded on a Varian 400 MHz and a Bruker 250 MHz spectrometer, EPR data on a Magnettech MS 200 CW X-band spectrometer at room temperature.

Results and discussion

A. Synthesis of a precursor with a 1 : 1 ratio of Zn to Cr

As chromium is well known to form half-sandwich complexes with benzene, a "Zn_4O_4" heterocubane with $Cr(CO)_3$ fragments attached to benzyloxy groups $[MeZnOCH_2PhCr(CO)_3]_4$ (**4**) is a promising target (Fig. 1). There are two reasonable routes

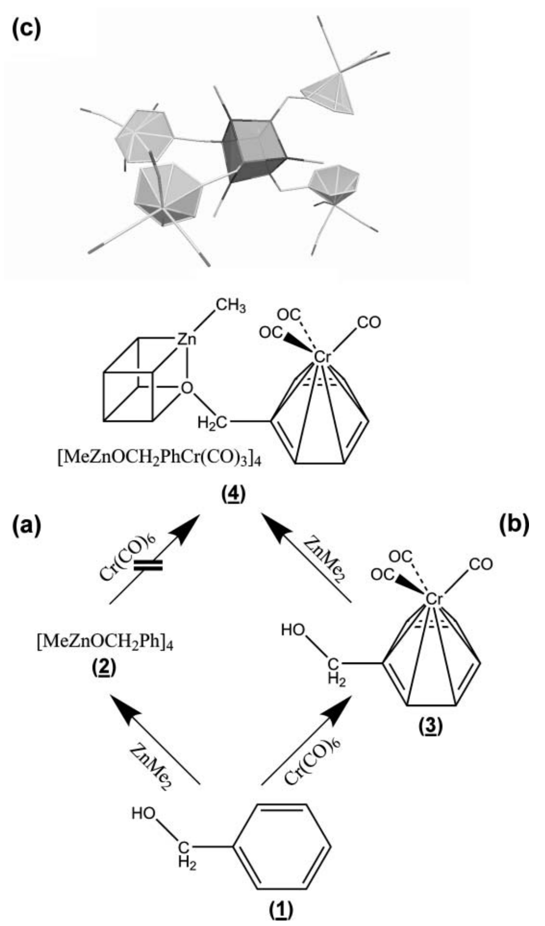


Fig. 1 Two possible routes (a, b) to the desired precursor compound (**4**) containing chromium and a "Zn_4O_4" heterocubane in one molecule. The structure of (4) as determined from single-crystal XRD is shown in (c).

(Fig. 1(a), (b)). The reaction between $Cr(CO)_6$ and the monometallic heterocubane $[MeZnOCH_2Ph]_4$ (**2**) is indicated in Fig. 1(a).

Although (**2**) was easily prepared by the reaction of benzyl alcohol (**1**) with dimethylzinc (see Experimental part and ESI SI-1†), its reaction with $Cr(CO)_6$ led to a mixture of products which were difficult to separate and to purify. Therefore, it appeared favorable to synthesize the tricarbonylchromium benzyl alcohol half-sandwich complex (**3**)[23,24] first (Fig. 1(b)), followed by reaction with $ZnMe_2$ to afford the desired bimetallic precursor (**4**) (Fig. 1(c)). The solubility of (**4**) is rather low in most organic solvents. Therefore, (**4**) tends to precipitate in the form of powders and it is very difficult to obtain single-crystals. Its structure determined from single-crystal X-ray diffraction shown in Fig. 1(c) is not very accurate due to the non-ideal quality of the crystals. Thus, the structure of compound (**4**) is reported here only as a partial determination (cell parameters $a = 36.38$ Å, $b = 8.20$ Å, $c = 20.44$ Å, $\beta = 114.13°$). Compound (**4**) contains a slightly distorted "Zn_4O_4" heterocubane building block. A methyl group is attached to each Zn^{2+}. The phenyl rings of the benzyl units coordinate to $Cr^0(CO)_3$ fragments in η^6 fashion. Therefore, besides its potential to act as a precursor for $Zn_xCr_yO_z$ materials, (**4**) is an interesting compound since it contains three different types of organometallic motives in one molecule: σ-type metal carbon bonds ($Zn–CH_3$; and Cr–CO) and π-type metal carbon bonds (Cr–Ph). In addition to the structural data determined from single crystal X-ray diffraction NMR data of compound (**4**) are given in SI-1.†

B. Materials formation from precursor (4)

The thermal decomposition of compound (**4**) was investigated using thermogravimetric analysis (TGA) and differential thermal analysis (DTA), shown in Fig. 2(a). The total mass loss Δm_{ges}(exp.) = −52.2% closely agrees with the mass loss expected for the formation of $ZnO{\cdot}Cr^{III}{}_2O_3$ (Δm_{ges}(th.) = −51.4%). Two main, exothermic steps are observed at 105 °C and 336 °C. The corresponding mass loss and comparison with TGA data of compounds (**2**) and (**3**) as references (see SI-2†) suggest that the CO and CH_3 groups are cleaved at very low temperature prior to the aromatic groups. To support the proposed mechanism, FT-IR spectra were recorded at different stages of the thermal decomposition (Fig. 2(b)). Significant changes are observed in the

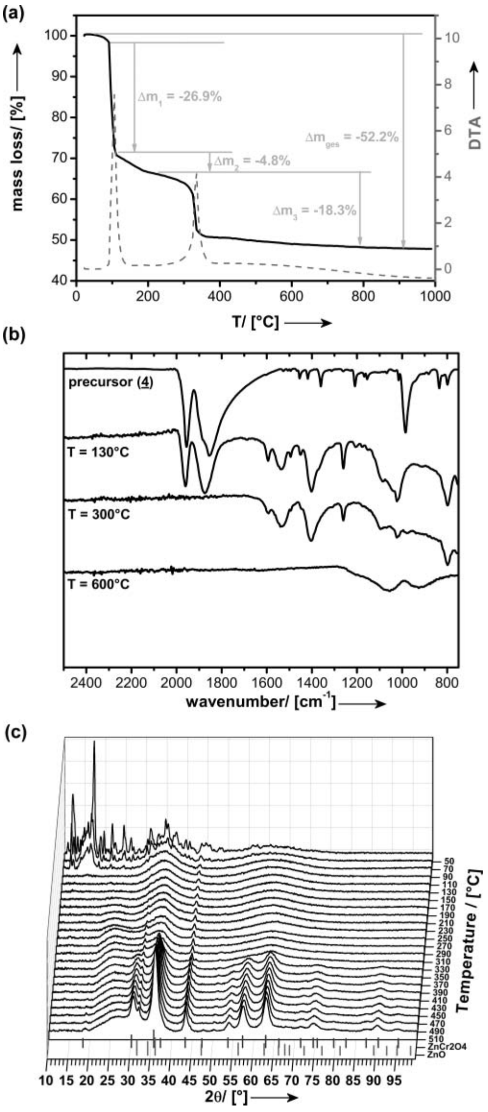


Fig. 2 Thermal decomposition of precursor (**4**) investigated by three independent analytical techniques: (a) TGA, (b) FT-IR and (c) *in situ* PXRD; the reference patterns of the two products ZnO and $ZnCr_2O_4$ are shown at the bottom of (c).

fingerprint region already at 130 °C. Although the bands which are characteristic for the CO groups (1961, 1874 cm^{-1}) are still present, their intensity in relation to the band at 985 cm^{-1}, which is typical for the aromatic system, has decreased. This indicates that Zn–CH_3 moieties have reacted with a fraction of the CO groups. At T = 300 °C all carbonyl ligands have been removed quantitatively. However, vibrations typical for aromatic systems are still discernible. Further insights into the transformation of the precursor to the materials state can be obtained from *in situ*, temperature-dependent powder X-ray diffraction (PXRD) shown in Fig. 2(c). The PXRD pattern of the precursor (**4**) is characterized by numerous reflexes in the region 10–55° 2θ. In good correlation to the TGA and FT-IR data, restructuring processes are apparently going on already at low temperature (T = 50–90 °C). In the region between 110 and 230 °C an entirely amorphous precursor phase is present. Then, at 250 C a small reflex appears at 31.7° 2θ, which indicates the formation of a ZnO phase. Finally, at 330 °C, the formation of the spinel $ZnCr_2O_4$ takes place.

Considering the TGA data it seems that the chromium atoms remain bound to benzene units up to 330 °C. As soon as Cr becomes available, $ZnCr_2O_4$ is the favoured product. The low temperature required for the formation of $ZnCr_2O_4$ is remarkable since in classical solid-state routes starting from ZnO and Cr_2O_3, temperatures of 900 °C are needed.[26] The final product of the precursor transformation is a mixture of the two phases (≈ 20% ZnO; ≈ 80% $ZnCr_2O_4$; see SI-3†). The results discussed up to this point demonstrate that one has to be very careful when precursors are used which contain within the same molecule groups of significantly different reactivity, and when, at the same time, the molecular composition does not coincide with the preferred product.

C. Synthesis of a precursor with a 1 : 2 ratio of Zn to Cr

Taking this into account, the phase-pure material ($ZnCr_2O_4$) should be obtained by using a precursor containing the two metals, zinc and chromium, in a ratio of 1 × Zn : 2 × Cr. The synthesis of such a precursor (**6**) was achieved as shown in Fig. 3. Similar to compound (**4**), unfortunately, only crystals of minor quality could be grown. Thus, the structure of compound (**4**) is reported here only as a partial determination (cell parameters a = 7.91 Å, b = 12.28 Å, c = 12.60 Å, α = 104.13° β = 95.29°, γ = 102.4°). Analysis of the new precursors by single-crystal X-ray diffraction shows that, due to the steric demand of the four benzyl tricarbonylchromium groups, a dimeric instead of a tetrameric form is preferred (Fig. 4(a)). Similar effects of the size of the alkoxy group on the nuclearity of alkyl-zinc alkoxides have already been reported by others.[27] Compound (**6**) behaves similar to (**4**) regarding its thermal decomposition behaviour (TGA data are given in SI-2†). Consequently, metal oxide formation was probed at two temperatures (350 °C and 1000 °C). As seen in PXRD (Fig. 4(b)), no ZnO phase has been formed as a side product and the spinel $ZnCr_2O_4$ is the only product.

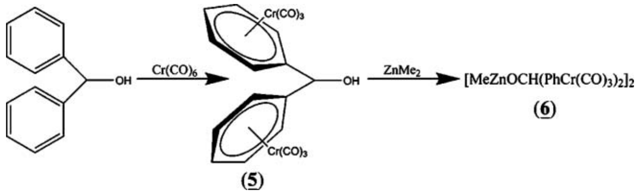


Fig. 3 Preparation of the new precursor (**6**).

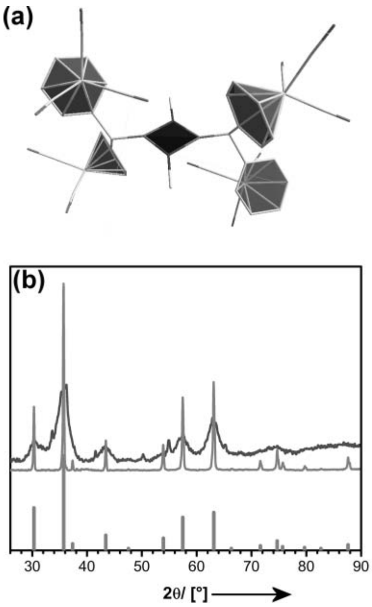


Fig. 4 (a) Structure of $[MeZnOCH(PhCr(CO)_3)_2]_2$ (**6**) as determined from single-crystal X-ray diffraction analysis. (b) PXRD patterns of products obtained *via* thermal treatment of (**6**) at T = 350 °C (top curve) and T = 1000 °C (bottom curve). The reference pattern of $ZnCr_2O_4$ is shown below.

D. Materials with low chromium content

Even though the preparation of the phase-pure spinel $ZnCr_2O_4$ was achieved by selecting a different precursor system, (**6**) instead of (**4**), one of the big disadvantages of bimetallic single-source precursors becomes evident: the range of accessible materials is severely restricted by the metal ratio in the precursor. Consequently, it is practically impossible to develop a single-source precursor system which is suitable for accessing the margins of a given phase diagram. As a single-source precursor leading to a ZnO material doped with 10% chromium (with respect to the metal atoms), for instance, one would need a multinuclear precursor compound containing exactly 9 × Zn centres and 1 × Cr centre. Not only would lower doping degrees quickly enlarge the number of necessary metal atoms per precursor molecule, for broken $M_1 : M_2$ ratios potential single-source precursors would become unattainably large.

For the soft-chemistry synthesis of oxide materials with adjustable contents of the two metals it is thus inevitable to apply mixtures of two different precursors in different ratios. To minimise the problem associated with the differing reactivity when using two different sources, it makes sense to use compounds which are chemically similar to each other. For the preparation of chromium-containing ZnO materials with low or fractional chromium content using precursors (**4**) or (**6**), for instance, the addition of a "Zn_4O_4" heterocubane as a source of pure ZnO is recommended. However, since the mentioned precursors are solids, it is difficult to ensure an atomic dispersion of the two precursors in the solid state. To solve this problem, we propose the following way. We have recently reported that an organometallic "Zn_4O_4" heterocubane $[MeZnOEtOMe]_4$ (**7**), which is a liquid at room temperature,[6] can fulfil two functions at once: it is a precursor for zinc oxide and it is a solvent. The advantage of using a solution of one precursor in the second precursor is that the highest possible degree of dispersion can be realized at the precursor state. Fig. 5 illustrates the synthesis of ZnO materials doped with low content of Cr^{III} obtained *via* the approach described above. Materials containing 0.05 to 0.5 at % Cr were prepared at $T = 350$ °C (see the experimental part). The resulting products were homogeneous powders showing a characteristic green colour (see SI-4†), which originates from an absorption maximum at $\lambda = 631$ nm, associated with Cr^{III} coordinated by oxygen in a tetrahedral environment.[28] UV-Vis spectra recorded in diffuse reflectance mode are shown in Fig. 6. The absorption due to the band-gap of the semiconductor ZnO appears in the UV-region. For the samples containing chromium, the band gap absorption is significantly red-shifted (by up to 35 nm) relative to pure ZnO. Assuming that the chromium centres represent true dopants, *i.e.* that they substitute the positions of Zn^{II} in the Wurtzite lattice, n-type doping would be expected. The additional donor-levels close to the conduction band (see SI-5†) would then explain the band-gap decrease.

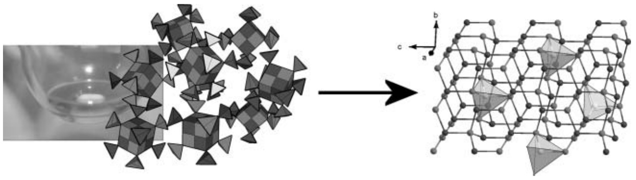


Fig. 5 Schematical representation of the approach taken for the synthesis of Cr^{III}-doped ZnO materials. The bimetallic precursor $[MeZnOCH_2PhCr(CO)_3]_4$ (**4**) is dissolved in the liquid "Zn_4O_4" heterocubane (**7**); see also Scheme 1. The transformation of such a solution into the respective metal oxide *via* soft-chemistry leads to a preservation of the vicinity of the four Cr centers in (**4**) also at the materials level.

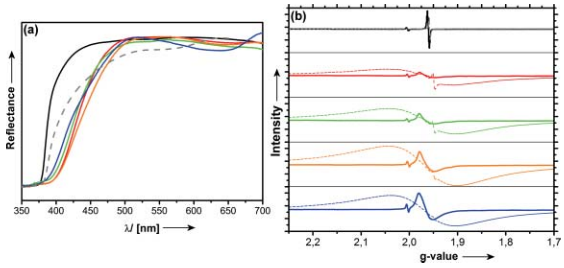


Fig. 6 (a) UV-Vis spectra, recorded in diffuse reflectance mode, for ZnO samples containing different amount of Cr^{III}: black curve → 0% (reference sample); red → 0.05_{at}%; green → 0.1_{at}%; orange → 0.25_{at}%; blue → 0.5_{at}%. The dashed grey curve was recorded from a sample containing 0.25_{at}% Cr which had been heated to 1000 °C. (b) EPR-spectra of Cr-doped ZnO materials prepared at 350 °C (solid lines) and 1000 °C (dashed lines).

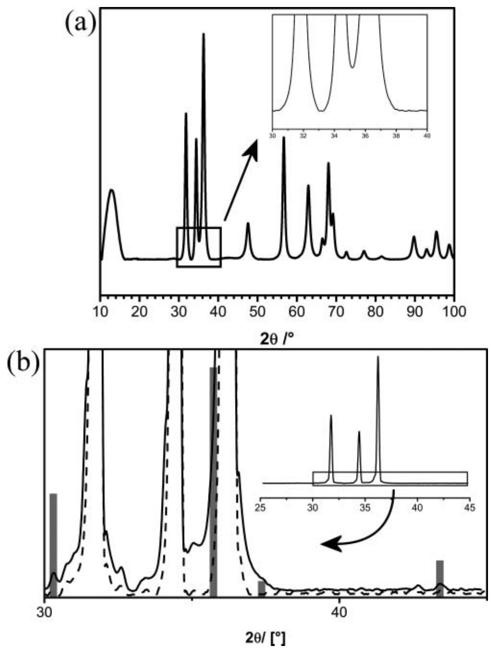


Fig. 7 (a) PXRD pattern of chromium containing ZnO prepared at low temperature (a; $T = 350$ °C) and high temperature ($T = 1000$ °C). The reference pattern of $ZnCr_2O_4$ is indicated as grey bars.

However, the optical data alone do not assure that the chromium has really substituted the zinc as illustrated in Fig. 5. Further analytical data were acquired for all samples mentioned. In PXRD, monophasic ZnO was found (diffractogram shown in Fig. 7(a)). There is one additional reflex at low angles ($2\theta = 12.9°$) which is indicative for the average distance of the Cr^{3+} centers in the ZnO matrix. Furthermore, for low chromium contents the expected intensities for a potential spinel phase might be relatively small. Therefore, the samples were also heated to 1000 °C to ensure formation of the thermodynamically stable products, *i.e.* a phase separation into $ZnCr_2O_4$ and ZnO. In the corresponding PXRD pattern (Fig. 7(b)) new but very small reflexes do indeed appear which can be assigned to $ZnCr_2O_4$. The changes in optical properties are more severe (Fig. 6(a)). The red-shift of the absorption at the band gap is much less pronounced and the absorption maximum in the visible region has shifted to $\lambda \approx 550$ nm due to the spinel formation and the change in Cr^{III} coordination. To probe for the local environment of the Cr^{III} centers in the ZnO matrix in further detail, X-band electron paramagnetic resonance (EPR) spectra were recorded for both types of materials (samples prepared at $T = 350$ °C and those treated at 1000 °C). Although pure ZnO is a diamagnetic substance, EPR signals are present in ZnO material prepared in absence of chromium. These EPR signals result from oxygen vacancies and carbon impurities as described in a previous publication and are not discussed here in further detail.[7,29] When Cr^{III} is present in the material, an additional signal appears at $g = 1.97$ with a width of ≈ 60 G. This *g*-value and coupling is in good agreement with findings reported in the literature for a weak interaction between Cr^{III} centres.[30] Isolated Cr^{III}-ions, which are supposed to give an EPR signal at around $g = 4.7$, were not detected in any significant amounts.[31] These findings suggest that a certain number of chromium atoms are indeed in vicinity to each other (Fig. 5), but do not form a separated secondary phase, in which the Cr ions are as close as, for instance, in $Cr^{III}–O–Cr^{III}$ contacts. Thus it appears possible to preorganize the degree of dispersion of the paramagnetic Cr^{III} centres on the molecular scale in the precursor compound. Precursor (**4**) contains four chromium atoms separated by a "Zn_4O_4" building block. It can thus be imagined that these chromium atoms remain relatively close to each other even when

(**4**) is dissolved in (**7**) and the chromium-doped ZnO is prepared *via* soft-chemistry (Fig. 5).

The latter aspect points to a new and interesting perspective: the spatial preorganization of magnetic moments in solid materials. The relevance of the soft-chemistry approach is demonstrated by considering the samples treated at 1000 °C. The signal at $g = 1.97$ ascribed to Cr^{III} ions appears now with a width of about 250 G. The enhanced peak broadening indicates stronger coupling between Cr ions that are now in close vicinity to each other, in agreement with the formation of the $ZnCr_2O_4$ phase. This comparison between low-temperature and high-temperature preparation of Cr-doped ZnO coherently underlines the advantages of the former method: precursors that can be transformed into metal-oxides at relatively low temperatures are necessary to ensure a homogeneous distribution of the dopant in the ZnO host matrix.

One final advantage of the approach presented here that more refined materials morphologies can be prepared easily. As proof of principle Cr^{III}-containing ZnO in the form of thin films can be prepared *via* spin-coating of the solution of precursors (**4**) in (**7**). The films were analyzed by atomic force microscopy (AFM) shown in Fig. 8. A scratch was created which allowed the determination of the thickness of the film which was ≈ 500 nm (Fig. 8(a)). The roughness of the film was measured at higher magnification. The film of composed of densely packed, slightly elongated nanocrystals. The roughness of the film is of the order of 5–10 nm according to height profile analysis.

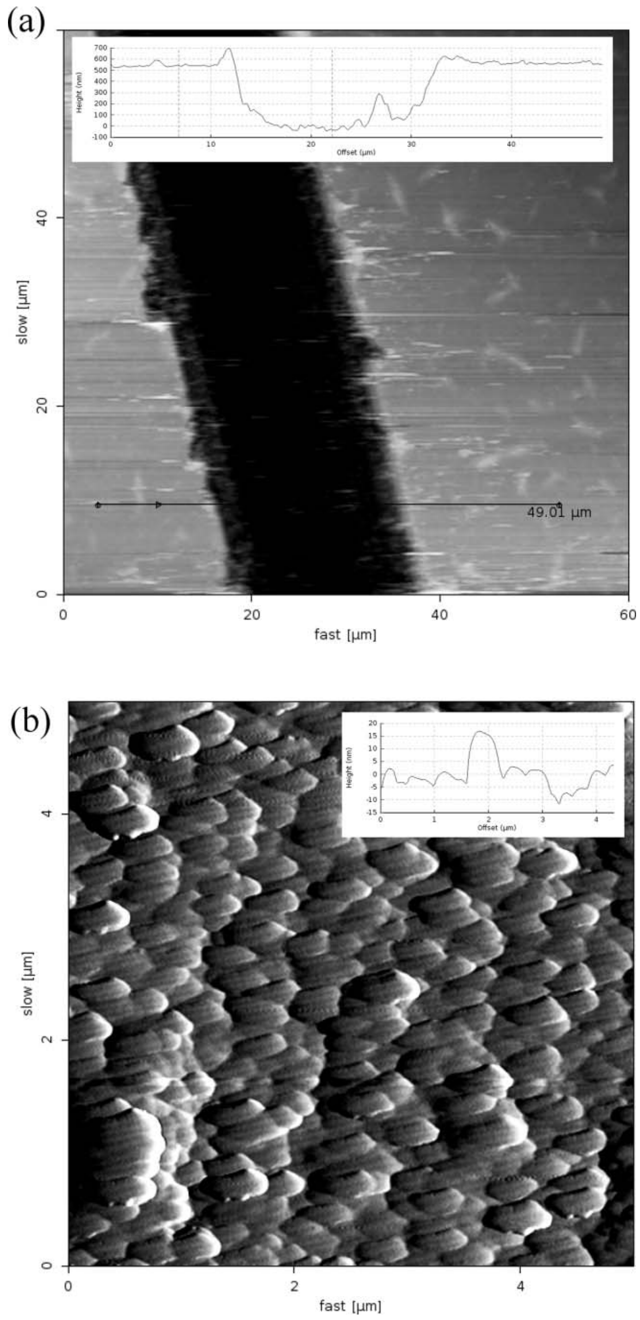


Fig. 8 Low magnification (a; recorded at a scratch) and high magnification (b) AFM images including height profile analysis of Cr containing ZnO films.

Conclusion

In summary, two new organometallic compounds containing Zn and Cr in ratios of 1 : 1 and 1 : 2 have been introduced for the synthesis of chromium-containing zinc oxide materials. The resulting materials ($ZnCr_2O_4$ and Cr-doped ZnO) represent interesting and functional solids. As shown above, it is possible to prepare the mentioned interesting materials at much lower temperature than with classical solid-state chemistry routes. One important parameter is the reactivity of the different parts present in the molecular source. If their reactivity is different, it is likely that the materials formation occurs in two steps and this can lead to a separation into the thermodynamically most stable phases. Under such conditions, phase separation can only be avoided if the metal content in the precursor is exactly identical to the content in the desired material. Furthermore it has been shown that it is nearly impossible to vary the metal content systematically using only a single source. If materials are required which contain a dopant metal either in low amounts or in a broken ratio, the use of a second precursor is inevitable. Even then the advantage of using a bimetallic single-source precursor is that the distribution of the second metal in the oxide matrix of the first metal can be controlled to a certain extend. Control over the distribution can be particularly interesting when it comes to magnetic phenomena associated with paramagnetic metals centers like Cr^{III} dispersed in a diamagnetic, semiconducting matrix such as ZnO.

Acknowledgements

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