

# Preparation and characterization of nanosized Zn–Co spinel oxide by solid state reaction method

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## Abstract

ZnCo<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·6H<sub>2</sub>O nanocrystal was prepared by a one-step solid state reaction method at room temperature under ambient conditions using oxalic acid as a chelating agent. Adding oxalic acid to the mixture of zinc acetate dihydrate and cobalt acetate tetrahydrate, grinding and subsequently calcining the precursor at different temperatures, the pink precursor was attained. Thermogravimetric analysis and differential scanning calorimetry have been used to study the thermal behaviors of the precursor, which reveal that the precursor is a compound. Powder X-ray diffraction data show that the sample obtained by heating the precursor between 350 °C and 550 °C for 3 h is a single-phase cubic material having the spinel-type structure, which can be confirmed by infrared spectra. Transmission electron microscopy images show that the grain size of the precursor and the products are about 50 nm and 20 nm, respectively.

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## 1. Introduction

Oxide spinel is a compound represented by general formula AB<sub>2</sub>O<sub>4</sub>, which comprises a very large group of structurally related compounds many of which are potentially attractive for use in technology [1]. Recently significant attentions have been paid to mixed oxides [2]. Cobalt-based spinel oxide has a strong catalytic activity to some reactions such as the oxidation reaction of the alkyl compounds [3], effective low-temperature absorbents of hydrogen sulfide [4]. Furthermore, nanosized ZnCo<sub>2</sub>O<sub>4</sub> is stable and active in alkaline solution and is more available and cheaper than noble metals (such as Pt, Ru, etc.) [5].

Traditional methods [6], for attaining complete reaction, a temperature of about 1000 °C (or higher) has to be maintained for several days [7], and does not always yield single-phase materials. Moreover, the products have relatively low specific surfaces and, accordingly, reduced efficiency in catalysis. Recently, some new methods have been proposed which

make it possible to obtain spinel oxides in the form of ultrafine or nanoscale particles, such as precipitation [8], sol–gel [9], sol–gel assisted coprecipitation [10], and microwave assisted hydrothermal method [1]. The conditions of these methods are complex and difficult to control, and the cost of industrialization is quite high. J.F. Xu et al. prepared monoclinic CuO nanoparticles by solid state reaction method [11]. In this paper we presented experiment results on ZnCo<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·6H<sub>2</sub>O nanoparticles prepared by a one-step solid state reaction method at room temperature. The method can provide a direct, single route to prepare nanosized oxide spinels, the formational temperature of Zn–Co spinel oxide is low. The most important is that the productivity effect and the purity of product can hardly access to 100%, which is any other methods especially for solution methods cannot match. The thermal stability of the cobaltites depends on the method for their synthesis [12]. So we investigated the thermal behaviors of the precursor by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), and characterized the end products and the precursor by transmission electron microscopy (TEM), X-ray diffraction (XRD), and IR techniques.

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## 2. Experimental

### 2.1. Materials

The calculated amounts of  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  (A.R. 99.0%) and  $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  (A.R. 99.5%) (molar ratio 1:2) with equimolar quantity of  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  (A.R. 99.8%) were mixed in the agate mortar and ground sufficiently for about 90 min. At the beginning of grinding there was a smell of acetic acid, kept on grinding till the mixtures became mash. The precursor powder was subsequently dried in a thermostatic oven at 40 °C for about 10 h, then the pink precursor was attained. The resulting material was calcined at 350, 450, 550, and 650 °C for 3 h, respectively.

### 2.2. Experimental apparatus

TG experiments were performed using a TGS-2 analyzer (Perkin-Elmer Co., America). Experiments were carried out in static air at heating rate of 10 °C  $\text{min}^{-1}$ . The sample mass in the Pt cell was kept at about 5 mg in all experiments, which can ensure a linear heating rate and accurate temperature measurements. The temperature of the furnace was programmed to rise from 30 °C to 700 °C. In order to prove the pink material to be a compound not to be a mixture, physical mixture of  $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  (molar ratio 1: 2) was investigated by TG in the same condition.

DSC experiment was performed using a Mettler-Toledo DSC822° (Switzerland) analyzer. The experiments were carried out in static air at heating rate of 10 °C  $\text{min}^{-1}$ . The sample (about 3.74 mg) was placed in the aluminum pan with a lid which was made a pierced hole. The reference pan was a pure aluminum pan. The temperature of the furnace was programmed to rise from 30 °C to 700 °C at heating rate of 10 °C  $\text{min}^{-1}$ .

XRD pattern for the precursor and the calcined samples were recorded at room temperature using a D8 (Bruker German) diffraction unit using a Cu target and Ni filter. The prepared products were identified by XRD employing a scanning rate of 0.05°/s in a  $2\theta$  range from 10° to 80°. The data were analyzed using JCPDS standards cards.

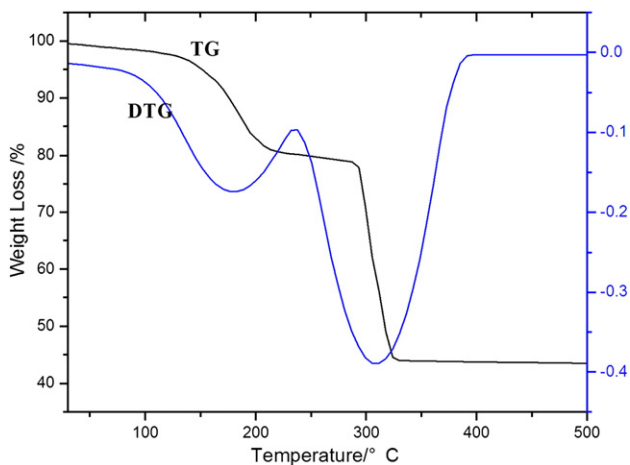


Fig. 1. TG/DTG curves of  $\text{ZnCo}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$ .

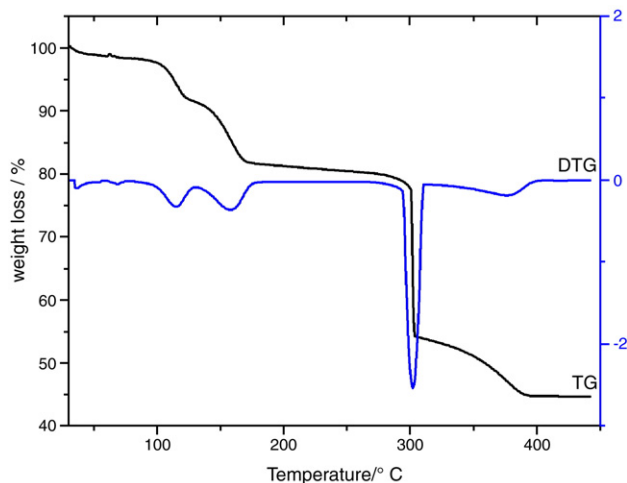


Fig. 2. TG/DTG curves of physical mixture  $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O} - 2\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ .

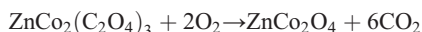
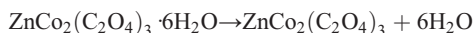
The morphology and dimension of the precursor and the calcined samples were observed using a FEI Tecnai G20 (FEI, Holland) TEM in an accelerating voltage of 200 kV.

IR infrared spectra were recorded in the range of 400–1400  $\text{cm}^{-1}$  on NICOLETNEXUS 470 Co. (USA) FT-IR spectrometer with KBr pellets. The infrared spectra were recorded at room temperature for the prepared products.

## 3. Results and discussion

### 3.1. TG

Fig. 1 shows the TG/DTG curves in static air at heating rate of 10 °C  $\text{min}^{-1}$  for nanosized  $\text{ZnCo}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$  and Fig. 2 shows the physical mixture  $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O} - 2\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ . It shows that the thermal decomposition of the precursor through two well-defined steps, the first step starts at 129 °C and ends at 218 °C, and is accompanied by a weight loss of 19.26% in accordance with calculated weight loss of 19.45% attributed for the dehydration of  $\text{ZnCo}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$  and the formation of anhydrous compound oxalate. The second step begins at about 298 °C and ends at 324 °C or so, the residue of this step is 44.19% in accordance with calculated residue of 44.53% due to the decomposition of  $\text{ZnCo}_2(\text{C}_2\text{O}_4)_3$  and the formation of the spinel oxide  $\text{ZnCo}_2\text{O}_4$ . From the TG data we can see that the experimental weight loss is in good agreement with the theoretical weight loss, and the thermal decomposition reaction produces the prospective  $\text{ZnCo}_2\text{O}_4$ . Comparing with the TG/DTG curves of the physical mixture  $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O} - 2\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , we can find that the thermal decomposition of the physical mixture via four well-defined steps, which mean the dehydration and the decomposition of the two metal oxalates are independent of each other. That is to say the precursor  $\text{ZnCo}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$  prepared by one-step solid state reaction method at room temperature is a compound. The theoretical weight loss occurring at each step is calculated from the equation below:



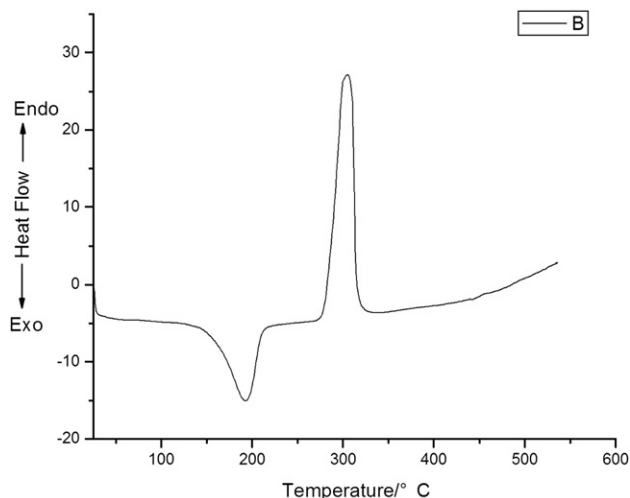


Fig. 3. DSC curve of  $\text{ZnCO}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$ .

From the thermogravimetric analysis we selected 350 °C as the lowest temperature for the calcinations process. Thus, the sample of the oxalate precursor was calcined at 350 °C, 450 °C, 550 °C, and 650 °C for 3 h.

### 3.2. DSC

DSC experiment was carried out in static air at heating rate of  $10\text{ °C min}^{-1}$ . Fig. 3 shows the DSC curve in static air at heating rate of  $10\text{ °C min}^{-1}$  for  $\text{ZnCO}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$ . Corresponding to the TG curve, the DSC curve also shows the decomposition of the  $\text{ZnCO}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$  through two processes. The endothermic peak at 192 °C is water release. The composite exothermic peak between 272 °C and 320 °C (Fig. 3) may be due to a number of processes, such as the oxidation of the oxalate group, liberation and oxidation of carbon monoxide, and the formation of the end product.

### 3.3. XRD

The XRD patterns of the precursor and the calcined products of the precursor at different temperatures in air for 3 h are shown in

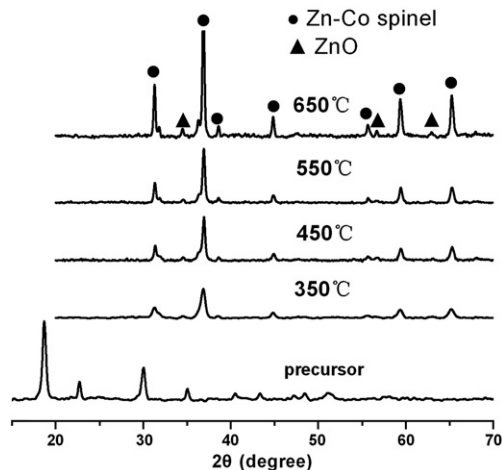


Fig. 4. XRD curves of the precursor and  $\text{ZnCO}_2\text{O}_4$  sample obtained at different temperatures.

Table 1

Experimental and JCPDS data diffraction peak positions, interplanar distance ( $d$ ) values of the cubic  $\text{ZnCO}_2\text{O}_4$  phase

Phase	( $h\ k\ l$ )	Experimental peak position $2\theta$	Literature interplanar distance $2\theta$	Experimental peak position $d$ (nm)	Literature interplanar distance $d$ (nm)
$\text{ZnCO}_2\text{O}_4$	2 2 0	31.206	31.215	0.28653	0.28630
	3 1 1	36.782	36.805	0.24414	0.24401
	2 2 2	38.525	38.489	0.23348	0.23370
	4 0 0	44.745	44.738	0.20237	0.20240
	4 2 2	55.567	55.570	0.16525	0.16524
	5 1 1	59.249	59.282	0.15593	0.15575
	4 4 0	65.147	65.149	0.14306	0.14307

Fig. 4. The XRD pattern of the precursor is in good agreement with literature [13] and the result of TG analysis, which can confirm that the precursor is  $\text{ZnCO}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$ . The precursor calcined at 350 °C shows the formation of Zn–Co spinel oxide, but the width of the diffraction peak is quite wide. As the temperature increases from 350 °C to 650 °C, we can find that the width of diffraction peaks decreases slightly and the intensity of the diffraction peaks increases. The experimental diffraction peaks (450 °C) and that of standard JCPDS card (JCPDS 23–13090) data are tabulated in Table 1. Seeing from the table, the experimental values and the literature values are similar, which confirm that the decomposition product is spinel-type oxide  $\text{ZnCO}_2\text{O}_4$ . When the precursor is heated at 650 °C, the XRD patterns take on impurity peaks. The sample obtained by calcination of the precursor at 350–550 °C is single-phase material and no impurities are observed in the resulting product. Compared to literature [13] the formational temperature of Zn–Co spinel oxide is lower. By the width of the XRD diffraction peak (311) and Scherrer equation  $d = \frac{k\lambda}{B \cos \theta} \frac{180^\circ}{\pi}$ , where  $d$  is the mean crystallite diameter,  $k$  (0.89) is the Scherrer constant,  $\lambda$  is the X-ray wave length (1.54056 Å), and  $B$  is the full width half maximum (FWHM), we obtained the following mean sizes of the nanocrystals: 14.36 nm (350 °C), 18.03 nm (450 °C), 25.05 nm (550 °C), 36.66 nm (650 °C).

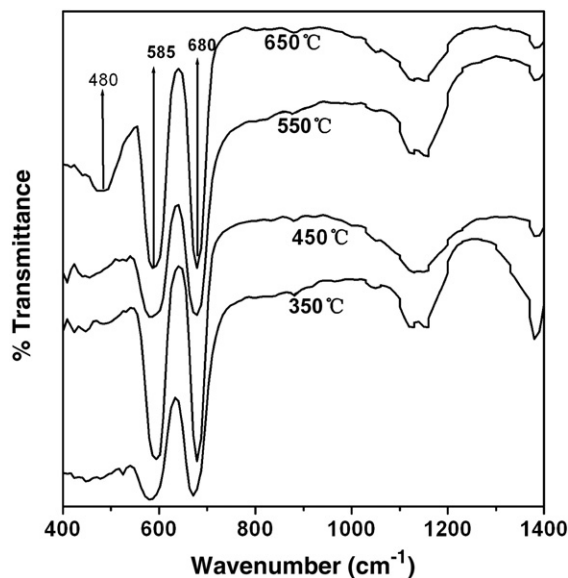


Fig. 5. FTIR spectra of  $\text{ZnCO}_2\text{O}_4$  sample obtained by heating at different temperatures: (a) 350 °C (b) 450 °C (c) 550 °C (d) 650 °C.

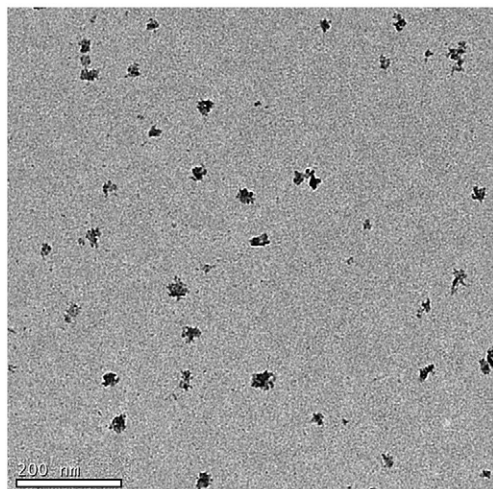


Fig. 6. TEM image of  $\text{ZnCo}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$ .

#### 3.4. IR

Fig. 5 shows the IR spectrum of the end products that are displayed in the range of  $400\text{--}1400\text{ cm}^{-1}$ . There are two absorption peaks at

$680\text{ cm}^{-1}$  and  $585\text{ cm}^{-1}$  respectively, corresponding to the M–O vibration frequency of the metal at tetrahedral clearance and octahedral clearance. They suggest that intensities of the bands increased from  $350\text{ }^\circ\text{C}$  to  $550\text{ }^\circ\text{C}$  as a result of increased crystallinity. XRD data confirm the formation of the perfect spinel structure. On further heating, the spectrum of  $\text{ZnCo}_2\text{O}_4$  shows weak absorptions in  $484\text{ cm}^{-1}$ , the band is characteristic of the ZnO phase. This suggests that Zn–Co spinel decomposes into two phase: ZnO and spinel containing less zinc cations.

#### 3.5. TEM

TEM images of  $\text{ZnCo}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{ZnCo}_2\text{O}_4$  particles are presented in Figs. 6 and 7. They show that the samples are composed of nanocrystals. The grain size of the precursor is about 50 nm, and that of  $\text{ZnCo}_2\text{O}_4$  sample calcined at  $350\text{ }^\circ\text{C}$  is only about 15 nm. It indicates that the nanosized particles are similarly spherical and well-proportioned. As the temperature increases, the grain size of the product becomes larger and the shape does not retain spherical. TEM study reveals that the particles are poorly crystallized and small when the calcinations temperature is low, reversely are well crystallized and larger. The TEM images are in good agreement with XRD data.

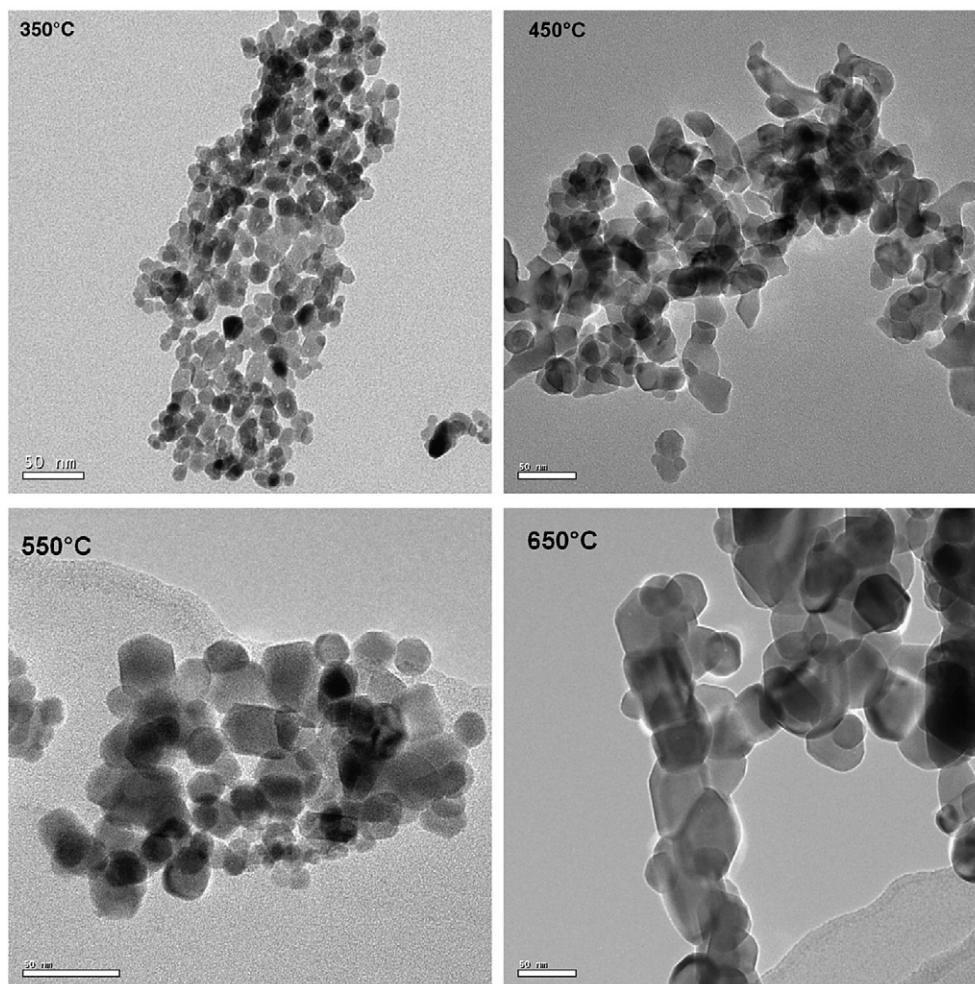


Fig. 7. TEM images of  $\text{ZnCo}_2\text{O}_4$  sample obtained by heating at different temperatures.

#### 4. Conclusion

Nanosized  $\text{ZnCo}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$  was prepared by one-step solid state reaction method at room temperature under ambient conditions, and characterized by TG, DSC, XRD, TEM and IR techniques. The results revealed that the precursor is a compound, and the grain size is about 50 nm. At 350–550 °C segment heating the precursor for 3 h is single-phase cubic material having the spinel-type structure, TEM image shows that the grain size of  $\text{ZnCo}_2\text{O}_4$  is about 20 nm. The characteristics of the obtained particles are the same as that obtained by coprecipitated method and traditional methods, but the formation temperature is lower and the particle size is smaller.

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