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Nanospinel mixed oxides obtained by self-propagating combustion. Blue cobalt aluminate

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Blue cobalt aluminate was obtained by self-propagating combustion from the system $2Al(NO_3)_3 \cdot 9H_2O$: $1Co(NO_3)_2 \cdot 6H_2O$: nNH_2CH_2COOH. The precursor was characterized by elemental chemical analysis, IR and UV-Vis spectra and thermal analysis. The $CoAl_2O_4$ spinel was characterized by the X-ray diffraction, TEM, IR and UV-Vis spectra.

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1. Introduction

Nanocrystalline metal oxides are going more and more interests during the past few years, since this new type of materials show properties, different from those of bulk material. Examples of improved properties are: lowered sintering temperatures, increased hardness, stability, special diffusion transport and ductility [1]. Aluminium based spinels constitute an interesting class of metal oxides with important technological applications. One example is the cobalt-aluminate spinel ($CoAl_2O_4$). It is well known as Thenard's blue for its impressive optical effect. Cobalt aluminate is widely used for the coloration of plastics, paint, fibers, paper, rubber, phosphor, glass, cement, glazes, ceramic bodies and porcelain enamels [2] and for catalytic applications in area such as the CO_2 reforming of methane [3]. In thin-film form, cobalt-aluminate is used as a light filters for automotive halogen lamps [4]. Synthesis routes play a crucial role in preparing the target product and determining its properties. $CoAl_2O_4$ spinel has been conventionally synthesized using solid state methods [5] which involve the mechanical mixing of metal oxides or hydroxides followed by a calcination at high temperatures above 1000 °C, for a long period of time as well as an extended grinding. Since 1980s, wet-chemical methods have been extensively applied to synthesize ultrafine $CoAl_2O_4$ spinel such as: coprecipitation method [6], hydrothermal synthesis [7], microemultion sol-gel synthesis [4,8,9]. Considerable efforts have been made to develop "soft chemistry" routes, in which polynuclear coordination compounds with two or more metal ions are formed as precursors. These compounds are capable to give nano-aluminates by thermal decomposition. Among them, there are the "complexation method" [10-12] and self-propagating combustion method [13,14]. The strategy for using glycine as fuel involves the complexation with appropriate metal ions. For this reason, we regard the combustion method as a thermal decomposition of polynuclear coordination compounds *in situ*.

In this research work, we investigate the synthesis of cobalt spinel-type aluminates obtained by self-propagating combustion method.

2. Experimental

2.1. Synthesis of complex compound precursor

All chemicals: $Al(NO_3)_3 \cdot 9H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ and glycine (NH_2CH_2COOH) were of reagent grade quality (Merck). The precursor-polynuclear coordination compound, $[Al_2Co(NH_2CH_2COO)_4](NO_3)_4 \cdot 3H_2O$, was prepared as follows: aluminium(III) nitrate, cobalt(II) nitrate and glycine were mixed in an agate mortar (in a 2:1:4 molar ratio) till a concentrate homogeneous was formed. The reaction solvent is the water hydration of nitrates, only. This solution is placed on P_4O_{10}. After 48 hours a purple-red solid was obtained. Anal. Calcd/Found: Al%:7.59/7.69;Co%:8.30/8.41;C%:13.5/13.25;N%:15.75/ 16.03; H%:3.09/3.02;Ox.%:24.89/25.01.

2. 2. Physical measurements

The polynuclear complex compound was characterized by elemental chemical analysis: the metal content was determined by atomic absorption technique; the carbon, nitrogen and hydrogen content were performed by microcombustion. IR spectra (400-4000 cm^{-1}) were recorded with a BIO – RAD FTIR 125 type spectrophotometer, in KBr pellets. Diffuse reflectance spectra (200-900 nm) were recorded at room temperature on a specord M-40 spectrophotometer, using MgO as standard. The thermal measurements (TG, DTG, DSC) were performed on a Netzch thermobalance STA 409 PC/PG type in a dynamic air atmosphere, with α-Al_2O_3 as

the inert reference compound. The crystalline phases in the calcinated powders were identified by XRD powder methods using a Rigaku-Multiflex X-Ray diffractometer (Cu K_α radiation). TEM images to determine the size and morphology of the cobalt aluminates were collected with an electronic microscope JEOL 200CX.

3. Results

The nature of precursors plays a very important role, in the synthesis of the nanomaterials. In many cases, the use of a particular precursor may affect the structure of materials at molecular level, thus improving the homogeneity and increasing the dispersion of resulted products [15]. We selected glycine because it acts as a complexing agent for a number of metal ions as contains a carboxylic acid group at one end and an amino group at the other end. On the other hand, glycine can also serves as a fuel during a combustion reaction, being oxidized by nitrate ions. From the system: 2Al(III) : 1Co(II) : nNH_2CH_2COOH, the following type of compound $[Al_2Co(NH_2CH_2COO)_4](NO_3)_4{\cdot}3H_2O$ was separated. The initial composition of the mixture containing aluminium and cobalt nitrates and glycine was derived from the total oxidizing and reducing valences of the oxidizer and fuel using the concepts of propellant chemistry [16]. The stoichiometric composition of the redox mixture needed is:

$$2(-15) + 1(-10) + n(+9) = 0,\ n = 40/9 = 4.4$$

Thus, the reactants were combined in the molar proportion 2:1:4.

4. Discussion

The formulae of this compound was established correlating elemental analysis with physico-chemical measurements (IR and UV-Vis spectra, thermal analysis). The IR spectrum of $[Al_2Co(NH_2CH_2COO)_4](NO_3)_4{\cdot}3H_2O$ (Fig. 1) was recorded and compared to that of glycine in the 400-4000 cm^{-1} range. The corresponding IR spectrum of glycine evidences the presence of two bands characteristic for carboxylic group ($\nu_{OCOasym}$ and ν_{OCOsym}), which supports the existence of glycine-zwitterion. In the spectrum of the $[Al_2Co(NH_2CH_2COO)_4](NO_3)_4{\cdot}3H_2O$ complex the band characteristic for the $\nu_{OCOasym}$ vibration shifts towards higher frequencies and the band assigned to the ν_{OCOsym} vibration towards lower frequencies. Thus, value of $\Delta\nu$~244 cm^{-1} suggests a monodentate bonding of this group to the metal ion. The presence of NO_3^- is supported by the existence of two bands ($\nu_{asym}(NO_3^-)$~1380 cm^{-1} and ($\nu_{sym}(NO_3^-)$~ 830 cm^{-1}) [17] (this band is completely overlapped with that due to ν_{OCOsym}).

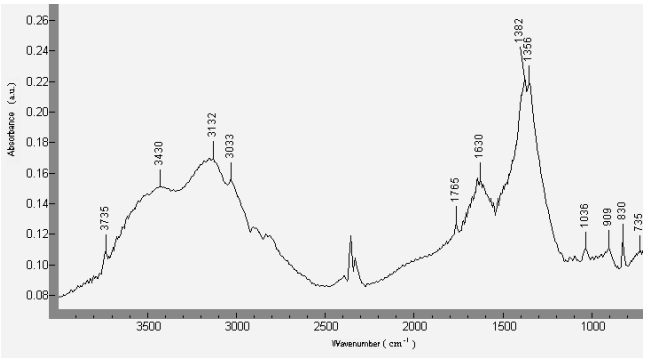


Fig. 1. IR spectrum of $[Al_2Co(NH_2CH_2COO)_4](NO_3)_4{\cdot}3H_2O$.

The diffusion reflectance spectrum recorded in the 200-900 nm range for the compound (Fig. 2, a) exhibits an absorbtion band at about 550 nm, which may be assigned to the $^4T_{1g} \rightarrow {}^4T_{1g}$ (P) (ν_3) transition, characteristic to Co(II) ion in a high-spin octahedral configuration.

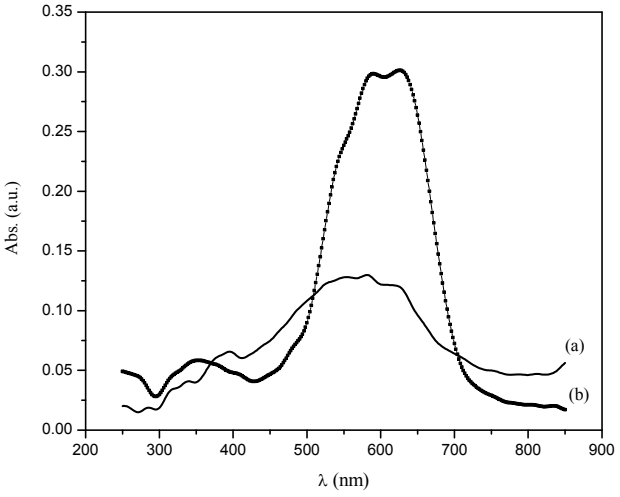


Fig. 2. Diffuse reflectance spectra: (a) $[Al_2Co(NH_2CH_2COO)_4](NO_3)_4{\cdot}3H_2O$ (b) cobalt aluminate spinel obtained by thermal decomposition of $[Al_2Co(NH_2CH_2COO)_4](NO_3)_4{\cdot}3H_2O$

A stepped decomposition is registered for the coordination compound in the temperature range (64 – 594 °C) (Fig. 3). A first decomposition stage (64 – 135 °C), characterized by a weight loss of 20.41 % and associated by an endothermic effect, is followed by a strong exothermic decomposition step (135 – 220 °C) with a weight loss equal with 48.58. The last decomposition stage (220– 800 °C) occurs with a linear decomposition rate, a weight loss equal with 10.37 being registered.

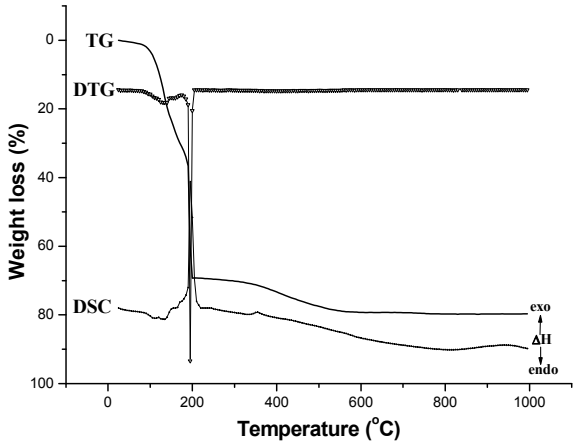


Fig. 3. Thermoanalytical curves (TG, DTG, DSC) of $[Al_2Co(NH_2CH_2COO)_4](NO_3)_4 \cdot 3H_2O$.

The $[Al_2Co(NH_2CH_2COO)_4](NO_3)_4 \cdot 3H_2O$ compound, was heated slowly on an incinerating dish at 100-150 °C. The compound ignites and burns within 5 minutes with a flame (flame temperature ~1000 °C). A dark-blue $CoAl_2O_4$ was obtained. In order to study the influence of the temperature on the spinel crystallite size, this compound was calcinated at two different temperatures: 800 °C/1 hr and 1000 °C/1 hr, respectively. After these treatments the dark-blue colour is converted into a light-blue one, well known as "Thenard's blue''. hese samples were analyzed by X-ray diffraction. The diffractogram indicated the formation of single-phase-$CoAl_2O_4$ spinel (Fig. 4).

To confirm the formation of spinel aluminate phase, the IR spectra of the final products (Fig. 5) were recorded in the 400-4000 cm^{-1} range. The spectra indicated the presence of three absorbtion bands at ~668 cm^{-1}, ~550 cm^{-1} and 502 cm^{-1}, respectively. These bands correspond to the formation of blue cobalt aluminate spinel [10, 11].

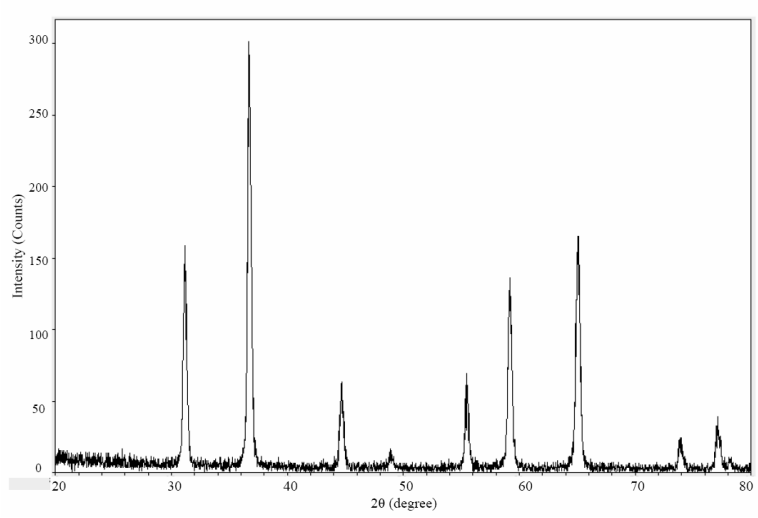


Fig. 4. XRD pattern of $CoAl_2O_4$ obtained by thermal decomposition of $[Al_2Co(NH_2CH_2COO)_4](NO_3)_4 \cdot 3H_2O$ after a heating treatment of 1000 °C/1 hr.

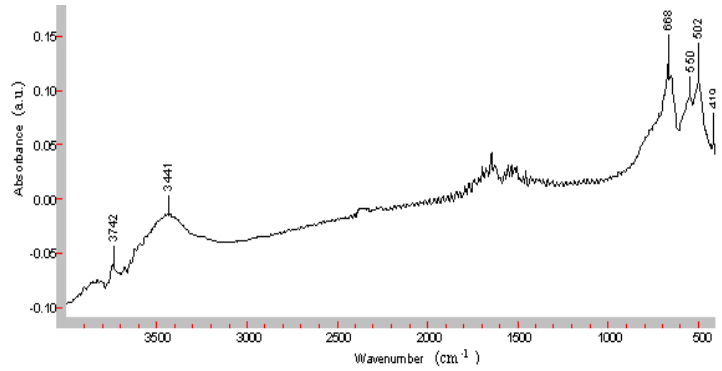
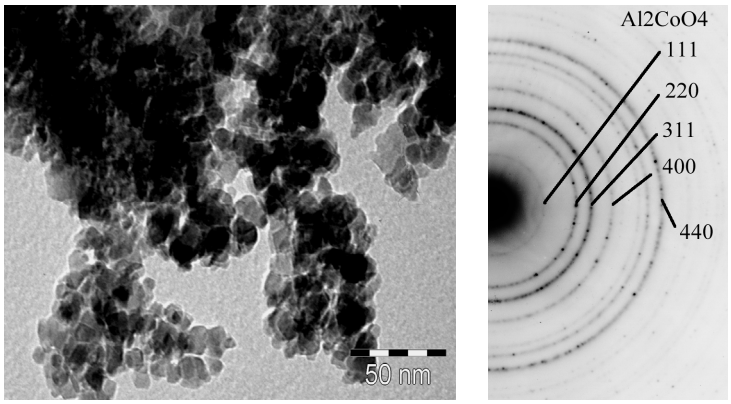
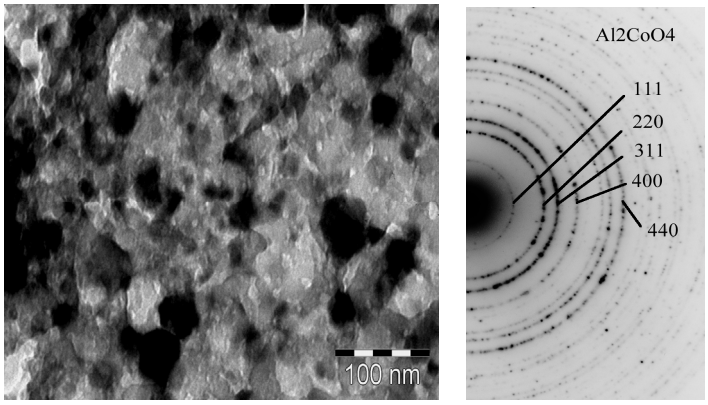


Fig. 5. The IR spectrum of cobalt aluminate obtained by thermal decomposition of $[Al_2Co(NH_2CH_2COO)_4](NO_3)_4 \cdot 3H_2O$ after a heating treatment of 1000 °C/1 hr.

The reflectance spectrum of $CoAl_2O_4$ spinel (Fig. 2, b) is characterized by a split broad absorbtion band. The intense absorbtion band with prominent peaks at around 590 nm and 650 nm, respectively, could be attributed to $^4A_2(F) \rightarrow {}^4T_1(P)$ (ν_3) transition and indicates tetrahedral coordination of Co^{2+} (d^7) ion.



(a)



(b)

Fig. 6. TEM image and the corresponding SAED pattern for the $CoAl_2O_4$ spinel obtained by thermal decomposition of $[Al_2Co(NH_2CH_2COO)_4](NO_3)_4{\cdot}3H_2O$ after a heating treatment of (a) 800 °C/1 hr and (b) 1000 °C/1 hr.

Fig. 6a displays the TEM images of $CoAl_2O_4$ spinel obtained by thermal decomposition of $[Al_2Co(NH_2CH_2COO)_4](NO_3)_4{\cdot}3H_2O$ after a heating treatment of 800 °C/1 hr. The spinel crystallites have a plate morphology with large (111) facets. For this reason the (220) and (440) reflexions appear stronger in the SAED pattern. The average size of the crystallites is about 10 nm. The crystallites form micron size aggregates. The TEM image and the corresponding SAED pattern for the $CoAl_2O_4$ spinel obtained by thermal decomposition of $[Al_2Co(NH_2CH_2COO)_4](NO_3)_4{\cdot}3H_2O$ after a heating treatment of 1000 °C/1 hr are shown in Fig. 6 b. The crystallite size is between 15 and 40 nm and the average size is about 25 nm. The crystallites are welded in large planar aggregates (micron size). Inter-grain voids are present in the aggregate volume. These voids have a size between 5 and 15 nm. The crystallite aggregate have some texture and the (440) reflexions is more intense like normal. Practically we observe the same texture like in the sample treated at 800 °C/1 hr.

5. Conclusions

In this work, Thenard's blue was prepared using the self-propagating combustion method. The precursor and the cobalt aluminate spinel were characterized by IR, UV-Vis spectroscopy, thermal analyses, X-ray diffraction and TEM. TEM images and SAED confirmed the nanocrystalline characteristics of the powders. The $CoAl_2O_4$ spinel particle average size increases from 10 nm to 25 nm with the enhancement of calcination temperature from 800 °C to 1000 °C.

References

[1] A. Edelstein,R. C. Cammarata, Nanomaterials: Synthesis, Properties and Applications, Institute of Pysics Publishing, Bristol, Philadelphia (1966).
[2] P. A. Lewis: Pigment Handbook, Vol. I, John Wiley and Sons, New York (1998).

[3] L. Ji, S. Tang, H.C. Zeng, J. Lin, K.L. Tan: Appl. Catal. A: General **207**, 247 (2001).
[4] U.L. Štangar, B.Orel, M.Krajnc, R.C. Korošec, P. Bukovec: Materiali in Thehnologije **36,** 387 (2002).
[5] P.H. Bolt, F.H.P. Habraken, J.W. Geus: J. Solid State Chem. **135,** 59 (1998).
[6] U. Chellan, Z.P. Xu, H.C. Zeu: Chem Mater. **12,** 650 (2000).
[7] Z.Z. Chen, E.W. Shi, Y.Q. Zheng, B. Xiao, J.Y. Zhuang: J. Am. Ceram. Soc. **86,** 1058 (2003).
[8] S. Chemlal, A. Larbot, M. Persin, J. Sarrazin, M. Sarrazin, M. Sghyar, M. Rafiq: Mater. Res. Bull. **35,** 2515 (2000).
[9] X. Duan, D. Yuan, Z. Sun, C. Luan, D. Pan, D. Xu, M. Lv: J. Alloy. Compd. **386**, 311 (2005).
[10] C. Wang, S. Liu, L. Liu and X. Bai: Mater. Chem. Phys. **96**, 361 (2006).
[11] C. Wang, X. Bai, S. Liu and L. Liu: J. Mater. Sci. **39** (2004), p. 6191
[12] C. Suciu, L. Patron, I. Mîndru, O. Carp: Rev. Roum. Chim. **51**, 385 (2006).
[13] T. Mimani, S. Ghosh: Current Science **78**, 892 (2000).
[14] W. Li, J. Li, J. Guo: J. Eur. Ceram. Soc. **23**, 2289 (2003).
[15] C. M. Simionescu, L. Patron, V. S. Teodorescu, M. Brezeanu, C. Capatana, J. Optoelectron. Adv. Mater. **8**(2), 597 (2006).
[16] Y.Zhang, G.C. Stangle: J. Mater. Res. **9,** 1997 (1994).
[17] K. Nakamoto: Infrared and Raman Spectra of Inorganic and Coordination compounds, Elsevier Publ. Comp., Amsterdam, London, New-York (1986).

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