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## Synthesis of cobalt aluminate spinel by sol-gel process: Investigation of starting reagents and precursors obtained after pyrolysis --Manuscript Draft--

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<b>Abstract:</b>	In this study, cobalt aluminate was prepared by a sol-gel method. XRD and FTIR analyses of the precursors obtained at 300 °C for 12 h revealed that the type of complexing agent used in the synthesis affects the pyrolysis step. An amorphous phase was obtained by using citric acid as the complexing agent. A beginning of crystallization was observed by using complexing agents such as polyacrylic acid and glycine. The structural investigation of the starting reagents revealed that the observed lines exhibit characteristics of Co <sub>3</sub> O <sub>4</sub> derived from cobalt nitrate. The crystallinity of the samples increased with the increase in the annealing temperature, with no effect observed by the change in the complexing agent. The appearance of the (331) reflection for the heat-treated powders was characteristic of the blue spinel compound.
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# **Synthesis of cobalt aluminate spinel by sol-gel process: Investigation of starting reagents and precursors obtained after pyrolysis**

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## **Abstract**

In this study, cobalt aluminate was prepared by a sol-gel method. XRD and FTIR analyses of the precursors obtained at 300 °C for 12 h revealed that the type of complexing agent used in the synthesis affects the pyrolysis step. An amorphous phase was obtained by using citric acid as the complexing agent. A beginning of crystallization was observed by using complexing agents such as polyacrylic acid and glycine. The structural investigation of the starting reagents revealed that the observed lines exhibit characteristics of  $\text{Co}_3\text{O}_4$  derived from cobalt nitrate. The crystallinity of the samples increased with the increase in the annealing temperature, with no effect observed by the change in the complexing agent. The appearance of the (331) reflection for the heat-treated powders was characteristic of the blue spinel compound.

**Keywords:** Pyrolysis; Cobalt aluminate; Complexing agent; XRD; FTIR.

## Specifications Table

Subject area	Materials science, soft chemistry, sol-gel
Compounds	CoAl <sub>2</sub> O <sub>4</sub> , Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O, Al(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O, C <sub>6</sub> H <sub>8</sub> O <sub>7</sub> ·H <sub>2</sub> O, (C <sub>3</sub> H <sub>4</sub> O <sub>2</sub> ) <sub>n</sub> , H <sub>2</sub> NCH <sub>2</sub> CO <sub>2</sub> H.
Data category	Synthesised, spectral and experimental.
Data acquisition format	TGA-DTA, XRD, FTIR.
Data type	Experimental and analysed.
Procedure	Cobalt and aluminium nitrates were mixed with stoichiometric proportions and then poured in excess into the solution of the complexing agents. The pH of the obtained mixture was adjusted to neutral by using ammonia. Evaporation, drying, pyrolysis and calcination processes allowing to produce the CoAl <sub>2</sub> O <sub>4</sub> precursors
Data accessibility	Data is available with this article

## 1. Rationale

Cobalt aluminate spinel is an inorganic pigment that is typically represented by the chemical formula  $\text{Co}^{2+}\text{Co}^{3+}_x\text{Al}_{2-x}\text{O}_4$ , where  $x = 0-2$ . This variation permits the possibility of obtaining different forms of the spinel structure, viz. a normal, an inverse or a mixed structure. The normal spinel structure of  $\text{CoAl}_2\text{O}_4$  is known for its blue colour. The inverse or mixed structure can exhibit different colours, and it changes from dark green and turquoise to blue depending on the replacement amount of  $\text{Co}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Co}^{3+}$  in the tetrahedral and octahedral sites [1–3]. The blue spinel of cobalt has attracted significant attention as a colouring agent in glaze and bulk tile compositions due to its superior properties, such as chemical and thermal stability as well as colour stability [4–8]. Furthermore,  $\text{CoAl}_2\text{O}_4$  nanoparticles exhibit good photocatalytic activity for the degradation of textile dyes [9,10].

Researchers have paid particular attention to the synthesis of cobalt aluminate systems via the investigation of preparation methods, processing control and firing temperatures [11–14]. The solid-state reaction method is the most widely used synthesis for cobalt aluminate systems, which involves the reaction of cobalt- and aluminium- based precursors. For example, cobalt oxide, cobalt hydroxide or others as a source of cobalt and aluminium oxide as a source of aluminium are used. The precursors are mixed in a stoichiometric amount followed by heat treatment at a minimum temperature of  $>1200^\circ\text{C}$ , affording cobalt aluminate [15–17]. This

method can be easily implemented and does not require a considerable amount of reagents. However, it generally affords powders with a poor homogeneity and a low specific surface. Other Synthesis methods, such as the sol-gel route, co-precipitation, combustion method and the hydrothermal route, have been developed to produce a powder of a good homogeneity and high purity at low temperature, with large specific surfaces [18–22].

Several factors have been considered to optimize the synthesis parameters. In previously reported studies, our group has reported the effect of the variation in pH for the synthesis and type of complexing agent on the texture of the powders obtained after heat treatment. These studies have reported that synthesis conducted in a neutral medium and using polyacrylic acid as the complexing agent leads to nanocrystalline  $\text{CoAl}_2\text{O}_4$  spinel powder [3,23]. In this study, particular attention was focused on the starting reagents and effect of chelating agents on the pyrolysis step during sol-gel synthesis.

## **2. Procedure**

The synthesis of the cobalt aluminate powder starts by mixing metal nitrates in stoichiometric proportions and pouring them into a solution containing an excess amount of complexing and chelating agents. Three samples were prepared using polyacrylic acid, glycine and citric acid as the complexing agents. The pH of the obtained solution was adjusted to neutral by using ammonia and subsequently heating to 80 ° C on a hotplate, affording a viscous gel. The gel was further dried in an oven at 120 ° C for 24 h, affording a xerogel. This xerogel was subsequently ground using an agate mortar and then placed in a muffle furnace adjusted to 300 ° C for 12 h. The precursors obtained after pyrolysis by using different complexing agents were analysed by X-ray diffraction (XRD) and Fourier infrared (FTIR) spectroscopy. By annealing, cobalt aluminate powder was obtained. Fig. 1 shows the schematic of the synthesis process.

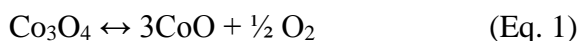
## **3. Data, value and validation**

Table 1 summarizes the characteristics of the reagents used in the synthesis. The metal nitrates were analysed and investigated individually by thermal analysis (TGA-DTA), XRD and FTIR analyses to study the thermal behaviour of the reagents used to prepare  $\text{CoAl}_2\text{O}_4$  oxide.

### 3.1. Study of starting reagents: $\text{Co}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$

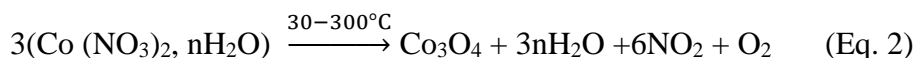
Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of hydrated cobalt nitrate (Fig. 2) revealed a total weight loss of ~74.3% in two steps:

- The first weight loss of ~72.5% is observed at temperatures of less than 300 ° C accompanied by endothermic effects, corresponding to the dehydration and loss of nitrogen oxide.
- The second weight loss of ~1.8%, accompanied by an endothermic peak, is observed at ~925 °C, corresponding to the partial transformation of cobalt oxide  $\text{Co}_3\text{O}_4$  into cobalt monoxide  $\text{CoO}$  according to the following reaction [24]:



The XRD diffractograms of the hydrated cobalt nitrate samples subjected to calcination at 300 °C, 500 °C and 900 °C revealed the sole formation of the oxide  $\text{Co}_3\text{O}_4$  (JCPDS n ° 76-1802), while the XRD spectrum of the sample subjected to calcination at 1100 °C revealed a mixture of  $\text{Co}_3\text{O}_4$  and  $\text{CoO}$  oxides ( Fig. 3). Fig.4 shows the FTIR spectra of the powders obtained after the calcination of cobalt nitrate at 300 ° C, 500 °C, 900 °C and 1100 °C. For all of the analysed powders, two absorption bands are observed at 662 and 572  $\text{cm}^{-1}$ , corresponding to the stretching vibrations of the metal–oxygen bond; this result confirmed the spinel structure of  $\text{Co}_3\text{O}_4$  [25–27]. Notably, it is extremely difficult to differentiate between the FTIR spectra of pure  $\text{Co}_3\text{O}_4$  and of  $\text{Co}_3\text{O}_4$  with  $\text{CoO}$  impurities [28].

The water content in hydrated cobalt nitrate sample used for synthesis is determined by its number of water molecules (n). TGA analysis (Fig. 2) revealed a weight loss of 72.5% in the temperature range of 40–200 °C. From the XRD spectra (Fig. 3), the lines observed for the sample subjected to calcination at 300 °C are characteristic of  $\text{Co}_3\text{O}_4$ . Therefore, the following decomposition reaction can be assumed [24]:

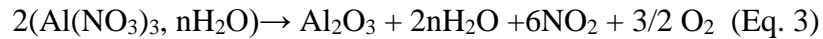


From this equation, which is based on TGA and XRD analyses, the experimental number n is calculated to be 6.06.

### 3.2. Study of starting reagents: $\text{Al}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$

Thermal analysis (DTA-TGA) of hydrated aluminium nitrate used in the synthesis revealed a total weight loss of ~86% (Fig. 5). DTA endothermic effects observed at a temperature of less than 450 °C are assumed to be related to the dehydration and elimination of nitrogen oxides [29,30]. A slight exothermic inflection is observed at ~870 °C, which is attributed to the formation of  $\gamma\text{-Al}_2\text{O}_3$ . By high-temperature treatment,  $\gamma\text{-Al}_2\text{O}_3$  is then transformed into  $\alpha\text{-Al}_2\text{O}_3$ . Fig.6 shows the XRD diffractograms of the hydrated aluminium nitrate subjected to calcination at different temperatures. The patterns of the samples obtained at 300 °C and 500 °C revealed an amorphous state. At 900°C and 1100°C, the XRD patterns revealed the crystalline phases of  $\gamma\text{-Al}_2\text{O}_3$  and  $\alpha\text{-Al}_2\text{O}_3$ , respectively (Fig. 6).

The n values were calculated on the basis of TGA-DTA and XRD analyses. In fact, for a weight loss of 86% in the temperature range of 40–900°C and from XRD diagrams (Fig.6), the following decomposition reaction can occur [31]:



The calculated n value from experiments is 9.15. Table 2 lists the numbers of molecules of water hydration (n) of the metal nitrates. The numbers calculated on the basis of TGA-DTA and XRD analyses are extremely similar to those provided by the suppliers.

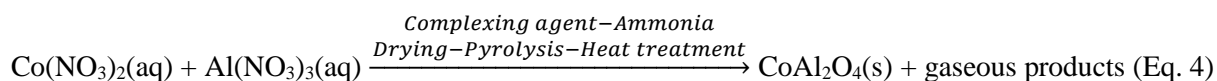
### 3.3. Synthesis of $\text{CoAl}_2\text{O}_4$ : Effect of the complexing agent on the precursors obtained after pyrolysis

The XRD diffractograms of the precursors obtained by using glycine and polyacrylic acid as the complexing agents revealed lines characteristic of a spinel phase (Fig.7 (a)). FTIR spectra revealed two characteristic bands of  $\nu_1$  and  $\nu_2$  in the range of 500–700  $\text{cm}^{-1}$ , corresponding to  $\text{Co}_3\text{O}_4$  oxide. In the case of citric acid, the XRD spectrum revealed an amorphous phase, and IR absorption bands are not observed in the range specific for oxides (Fig 7(b)). The IR absorption band observed at ~1610  $\text{cm}^{-1}$  corresponds to the carboxylic groups resulting from citrates during pyrolysis. This result can be explained by incomplete decomposition. The bands observed

between 1400 and 1500  $\text{cm}^{-1}$  for the three precursors correspond to the nitrate ions ( $\text{NO}_3^-$ ) [32,33].

### 3.4. Synthesis of $\text{CoAl}_2\text{O}_4$ : heat-treatment

The powders obtained at 300 °C for 12 h (pyrolysis) were subjected to heat treatment at 500 and 900 °C. The obtained diffractograms revealed that the intensity of XRD patterns increases with the increase in temperature, indicative of the evolution of the crystallinity of the powders (Fig.8). The pure cobalt aluminate phase is characterized by the appearance of the (331) reflection [17,34–36]. The synthesis conditions (including type of complexing agent, calcination temperature, synthesis pH) were examined and applied in our recent study [3,23]. Results revealed that the cobalt aluminate oxide is obtained at 900 °C whatever the pH and the nature of the complexing agent used. The synthesis process of cobalt aluminate spinel can be represented as:



## 4. Conclusion

The characterization of the starting reagents responsible for the formation of  $\text{CoAl}_2\text{O}_4$  strengthens the investigation into the effect of the change of complexing agents at the pyrolysis stage. By the mixing of nitrates in the presence of citric acid as the complexing agent with the addition of ammonia for pH adjustment, followed by pyrolysis, an amorphous phase is obtained, which can be explained by the incomplete decomposition of the organic constituents. However, by using glycine and polyacrylic acid, the start of crystallization, with lines characteristic of cobalt oxide, is observed. Subsequent heat treatment affords cobalt aluminate.



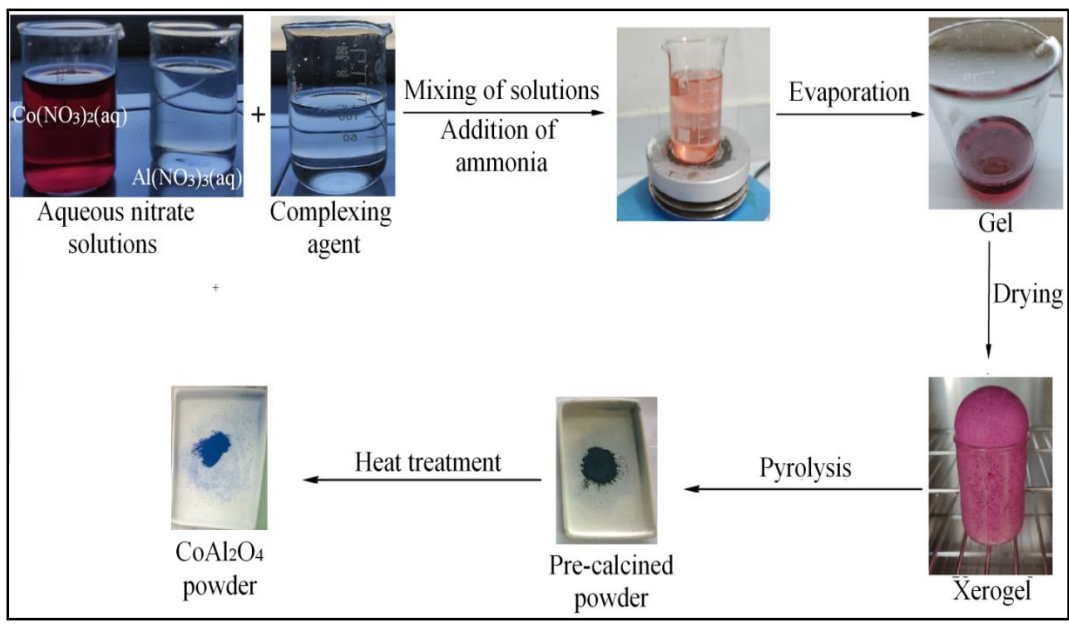
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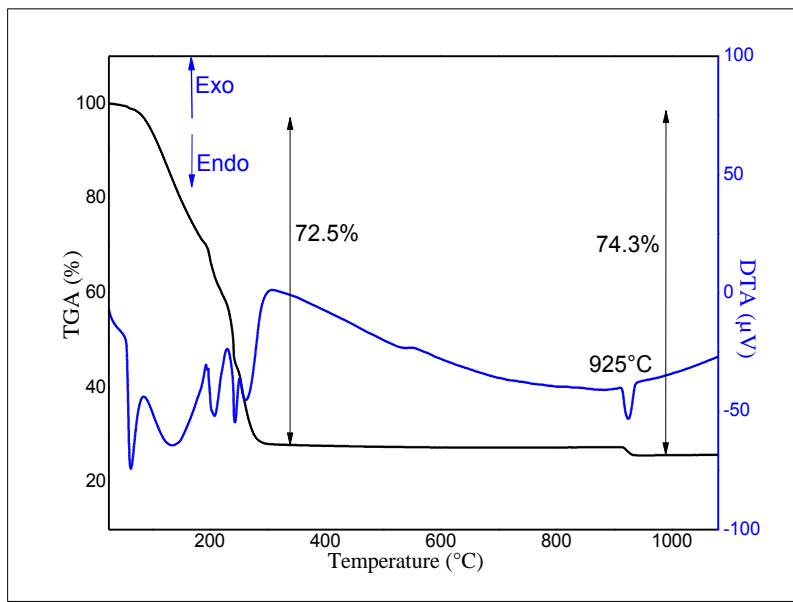
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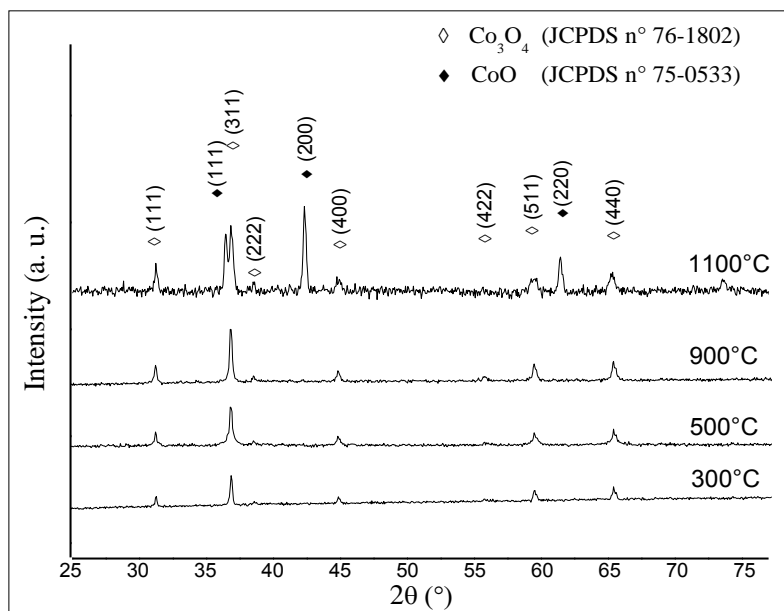
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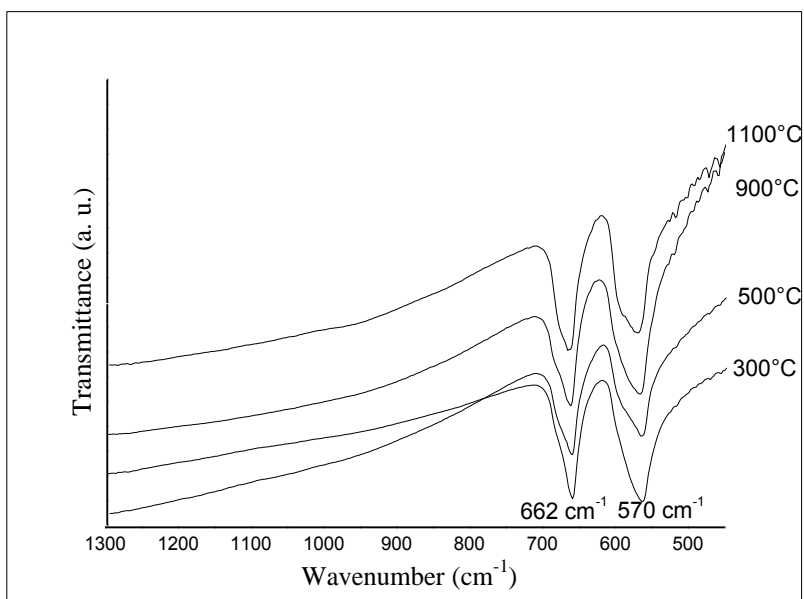
**Fig.1.** The schematic illustration of synthesis of cobalt aluminate powder by sol-gel synthesis.



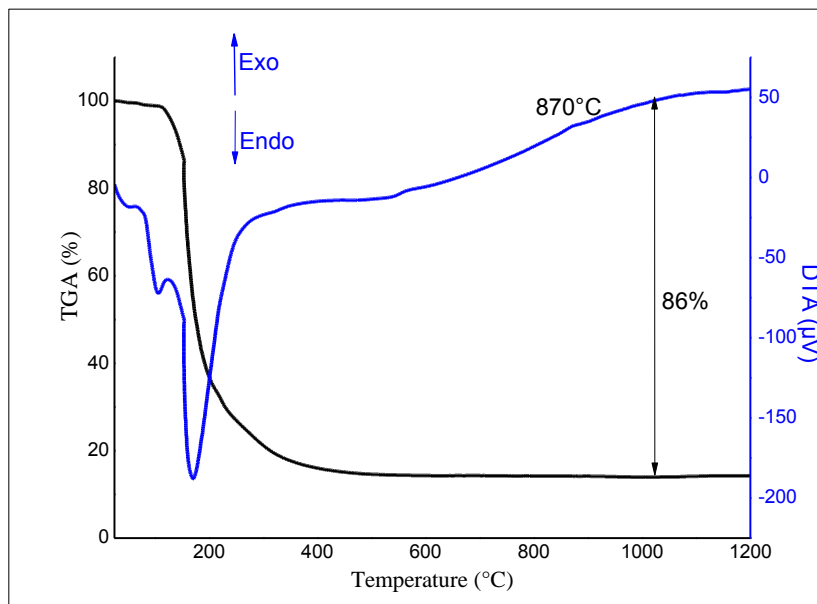
**Fig. 2.** DTA and TGA curves of hydrated cobalt nitrate ( $\text{Co}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ ).



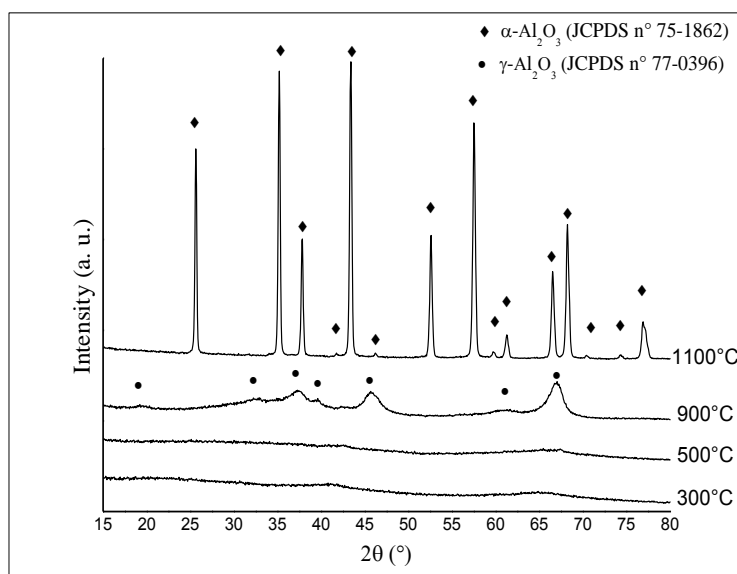
**Fig. 3.** X-ray diffraction patterns of cobalt nitrate calcined at 300 °C, 500 °C, 900 °C and 1100 °C.



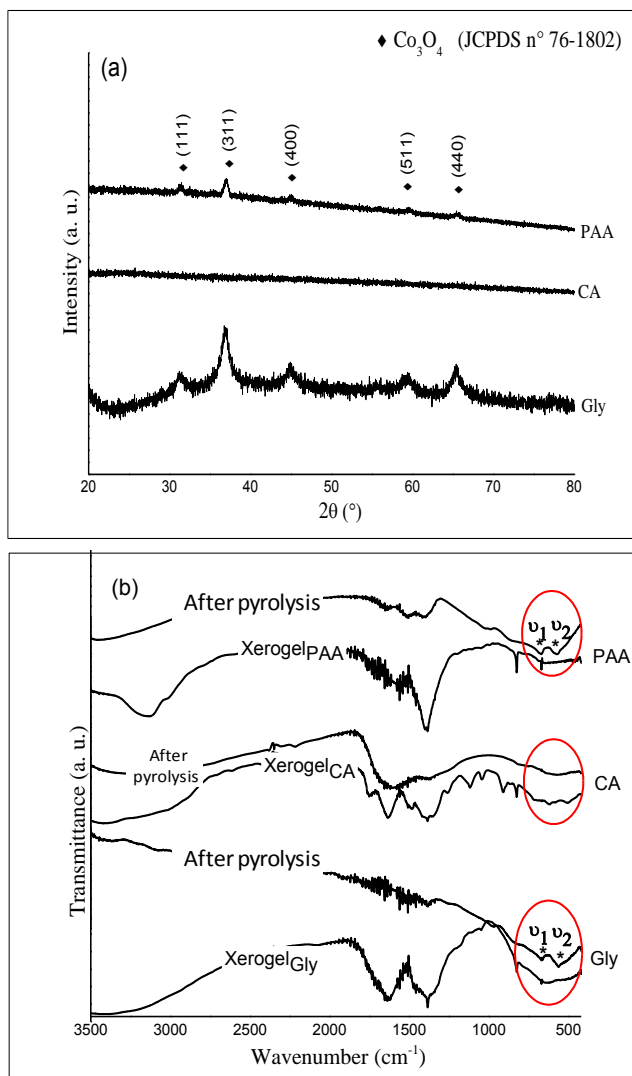
**Fig. 4.** FTIR infrared spectra of cobalt nitrate calcined at 300 °C, 500 °C, 900 °C and 1100 °C.



**Fig. 5.** DTA and TGA curves of hydrated aluminium nitrate.

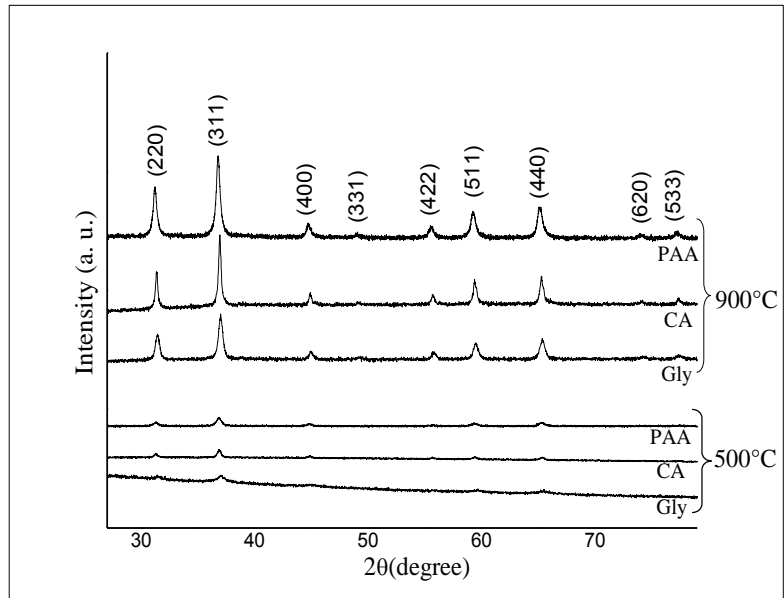


**Fig. 6.** XRD diffractograms of calcined aluminium nitrate at 300 °C, 500 °C, 900 °C and 1100 °C



**Fig.7.** (a) XRD patterns and (b) FTIR analysis of the precursors obtained after pyrolysis





**Fig.8.** XRD patterns of the samples obtained after pyrolysis and heat-treated at 500°C and 900°C.

**Table 1**

Characteristics of the reagents used for the synthesis.

Chemical reagents	Molecular Weight (g/mol)	Assay (purity)	Manufacturer	Concentrations and molar ratios used in the synthesis
Cobalt nitrate, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	291.03	99.0 %	Sigma Aldrich	0.2M
Aluminium nitrate, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	375.13	99.0 %	Sigma Aldrich	0.2M
Glycine, $\text{H}_2\text{NCH}_2\text{CO}_2\text{H}$ (Gly)	75.07	99.0 %	Aldrich	Gly/ $\text{NO}_3^- = 2/3$
Citric acid, $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ (CA)	210.14	99.5%	Panreac	CA/cations=3
Polyacrylic acid, $(\text{C}_3\text{H}_4\text{O}_2)_n$ (PAA)	1800	99.0 %	Sigma Aldrich	10 wt%

**Table 2**

Numbers of water molecules in the hydrated salts used in the synthesis.

Hydrated salts	n experimental	n indicated on the bottle label
$\text{Co}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$	6.06	6
$\text{Al}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$	9.15	9

## **Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: