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A LOW TEMPERATURE PATH TO THE PREPARATION OF $CoFe_2O_4$ FERRITE[*]

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Ultrafine cobalt ferrite has been prepared by the decomposition of cobalt oxalate-hydrazinate complex, which is used as precursor. The preparation and thermal decomposition of the precursor have been studied using chemical, thermal, and infrared techniques. The precursor decomposes at low temperatures with the effusion of large amounts of gases. The coordination compounds used as chemical precursors have to include, ligands, which generate, by decomposition, volatile products. Carboxylic acids are ligands, which correspond to this requirement. It is well known that the time required for thermal decomposition of oxalates can be considerably shortened if the precursors are heated in the presence of a reducing agent, such as hydrazine. The hydrazine together with cobalt cations have been incorporated in the structure of iron oxalate for yielding coordination compounds, chemical precursors for low temperature synthesis of the corresponding ferrite. For cobalt oxalate-hydrazinate it was established the chemical composition, spectral properties and thermal behaviour to determine the conditions for ferrite powder synthesis. Chemical, infrared, and Mössbauer spectroscopy confirmed the formation of spinelic ferrite, at 500 ^oC.

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1. Introduction

Physical, chemical and structural properties of oxide powders depend on preparation method and on the applied thermal treatment [1,2]. Therefore, in the last time, considerable efforts have been made to develop a synthesis method for oxide powders from chemical precursors.

Such a method seems to be the method of the thermal decomposition of coordination compounds.

Compared to the classical methods for synthesis of oxide powders that involve repeated firings of the component oxides, hydroxides or carbonates at high temperatures with frequent grindings and mixings, the precursor method offers some advantages:

-the decomposition of coordination compounds is simultaneous with (or followed immediately by) formation of a mixed oxide;

-the temperature of formation of mixed oxide is much lower than sintering or calcination temperature of some mechanical mixtures of single oxides;

-thanks to the relatively low temperature of formation, the mixed oxides obtained are characterised by fine granulation, high specific surface area and porosity (features that are very important for the catalytic activity of oxides);

-the homogeneity at molecular scale;

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-a lower content of impurity.

The coordination compounds used as chemical precursors have to include ligands that generate, by decomposition, volatile products. Carboxylic acids are ligands that correspond to this requirement. It is well known that the time required for thermal decomposition of oxalates can be considerably shortened if the precursors are heated in the presence of a reducing agent, such as hydrazine [3].

The hydrazine can run as unidentate and bidentate ligand due to the variety of ways in which it may be bounded. Thus, there are a very large number of its derivatives.

About oxalate hydrazinate complexes the literature is relatively poor [4]. Only oxalate hydrazinate of Fe was studied and published [5]. In this context, chemical analyses and establishes chemical composition of the complex is very important.

The purpose of our study was the incorporation hydrazine together with metallic cations in the structure of some oxalates for yielding coordination compounds, chemical precursors for low temperature synthesis of oxide powders. It was obtained oxalate hydrazinate complex of Fe and Co. For this compound it was established the chemical composition, spectral properties and thermal behaviour in order to determine the conditions for ferrite powder synthesis.

2. Experimental

2.1. Synthesis of Co-Fe oxalate hydrazinate complex

A wet chemical method was adopted to prepare Co-Fe oxalate hydrazinate complex. Ammonium oxalate and a solution of hydrazine hydrate in a 1:3 molar ratio were mixed and stirred under a nitrogen atmosphere at 80 ^{0}C for one hour to provide ammonium oxalate hydrazinate. A saturated mixture of cobalt and ferrous chloride solutions in a 1:2 molar ratio was added slowly to the ammonium oxalate hydrazinate complex in a 1:1 molar ratio to obtain an tawny precipitate of cobalt and ferrous oxalate hydrazinate complex. The precipitate was washed, filtered, and dried at 70 ^{o}C to avoid the thermal decomposition. Heated in air at 260 ^{o}C, the precursor decomposes exothermic producing a fine, crystalline powder of oxide ceramic material. This material was analysed after a thermal treatment at 500 ^{o}C, in air, for one hour. The product has the chemical formula $CoFe_2O_4$.

2.2. Characterisation of Co-Fe oxalate hydrazinate complex and ferrite powder

For the characterisation of polynuclear complexes of oxalate hydrazinate it is necessary a complex analytical system capable to elucidate the mechanism of the reaction, to determine the composition and the properties of the substances. The analytical systems that help us to resolve these problems contain chemical analysis, IR spectrometry and thermal analyses. Each of these methods supply only one part of information and together give a good image of the phenomena and the properties. Thus, chemical analyses were necessary to determine the composition and properties of the complexes while IR and spectrometry give informations on the nature of the chemical bonds.

Chemical analyses were used to determine the composition of the complex. Cobalt and iron were determined volumetrically. Hydrazine and oxalate content were calculated with the values by elementary analyses (the content of nitrogen, hydrogen and carbon).

Infrared spectra of the complex were recorded on a FTIR Shimadzu 8201 PC spectrophotometer using the pilling technique in KBr from 350 to 7800 cm^{-1}.

Thermal analyses of Co-Fe oxalate hydrazinate complex were performing using simultaneous TG-DTG. The experiments were performed under ambient atmosphere and nitrogen atmosphere with a heating rate of 20 ^{o}C/min, on a TGA V_5 DuPont 2000 instrument.

The Mössbauer spectrum of ferrite powder was recorded on electromechanical spectrometer, at room temperature, with ^{57}Co/Cr source (20mCi activity), and standard α-Fe.

The shape and the particle size of the ferrite were determined by electron microscopy. The ferrite powder was studied with the electronic microscope TESLA BS 301. The samples were prepared by dried method (dispersion on the support).

3. Results and discussion

All results show that a compound with a crystalline structure and chemical formula: $CoFe_2.3C_2O_43\text{-}N_2H_4.6H_2O$ was obtained.

The result of the chemical analyses of oxalate hydrazinate synthesised is presented in table 1.

Table1. Chemical analysis of Co-Fe oxalate-hydrazinate.

Analyzed	Content (%)
Co	9.1
Fe	17.2
Oxalate	40.9
Hydrazine	14.9

The characteristics of some atoms and groups of atoms, as regarding the chemical bonds, are evidenced by IR spectrometry. The number of active vibration modes in IR depends on both groups of symmetry and type of realised bond [6].

FTIR spectrum was recorded in 350 - 7800 cm^{-1} range. The FTIR spectrum of Co-Fe oxalate hydrazinate has a broad band in the region 3100 - 3500 cm^{-1} with peak position at 3380 cm^{-1}. The complex has bands at 824 and 1318 cm^{-1} due to δ(O-C-O) and ν_s(O-C-O), respectively. Among 420 - 490 cm^{-1} the spectrum has a band allotted to ν(M-O), where M is Co or Fe. The presence of hydrazine is noticed among 1070 - 1130 cm^{-1} due to δ(NH2) and at 972 cm^{-1} due to ν(N-N). Consequently, we conclude that our complex has a polymeric structure with bridging hydrazine since the N-N stretching frequency is at 970 - 980 cm^{-1} that is assigned to ν(N-N) of bidentate hydrazine [7-9].

The IR spectrum is shown in Fig. 1.

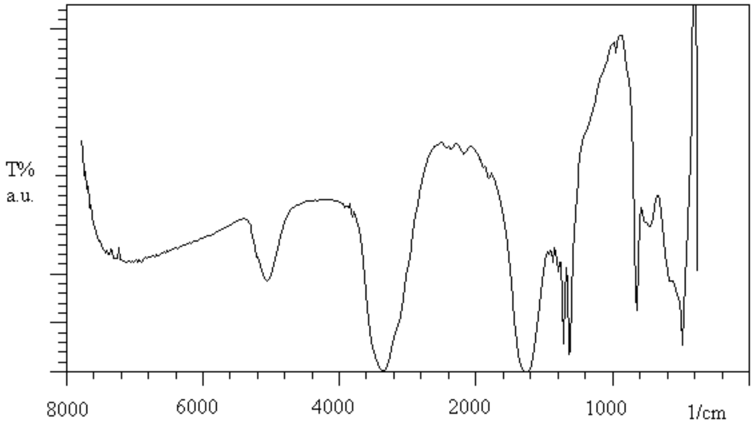

Fig. 1. FTIR spectrum of Co-Fe oxalate hydrazinate.

Thermal stability of Co-Fe oxalate-hydrazinate was studied by thermogravimetry in air and nitrogen atmosphere. The TG/DTG curve presents a rather straightforward degradation in air (Fig. 2) as well as in an inert atmosphere (nitrogen, Fig. 3). When the TG curve were recorded in air, the steps of decomposition were obtained at much lower temperature that in nitrogen atmosphere. The rate of decomposition in nitrogen atmosphere is much lower than in air but the weight loss is comparable at 500 ^{o}C.

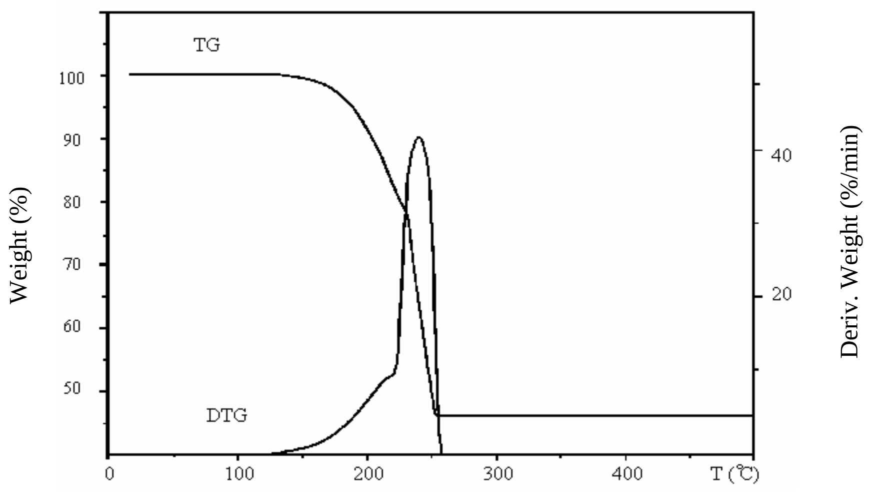

Fig. 2. TG-TTG curves, in air, for Co-Fe oxalate hydrazinate complex.

TG and DTG curve shows two steps of decomposition reaction in both atmospheres. After 260 ^{o}C, the system is stable from the point of view of the weight loss and of its energy when the decomposition is in air. In nitrogen atmosphere is stable after 430 ^{o}C.

TG-DTG curves recorded in air for Co-Fe oxalate hydrazinate complex are presented in Fig. 2. The thermal behaviour of Co-Fe oxalate hydrazinate complex in nitrogen atmosphere is seen in Fig. 3. The nitrogen atmosphere moves the decomposition temperature upwards, for all steps of decomposition.

The thermal decomposition put into evidence that the design of molecular structure allowed for the decomposition of Co-Fe oxalate-hydrazinate to the corresponding ferrite in air (55%) as well as in nitrogen atmosphere (56%).

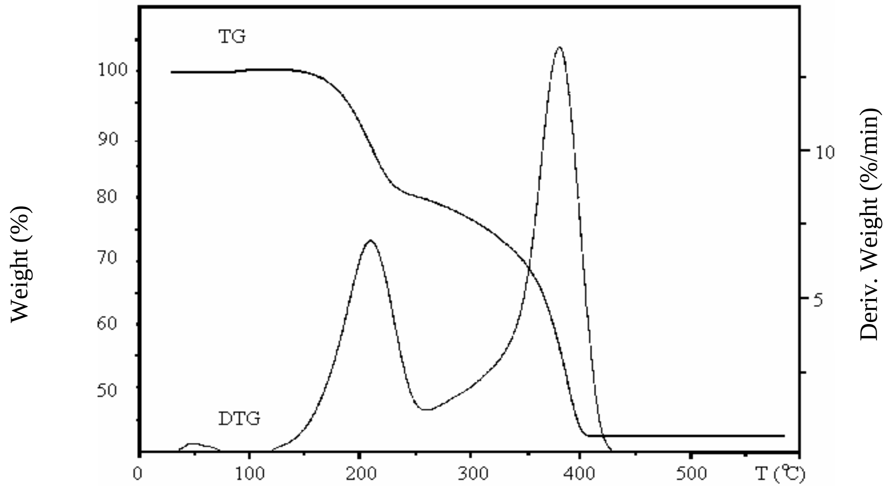

Fig. 3. TG-DTG curves, in nitrogen, for Co-Fe oxalate hydrazinate complex.

The ferrite powder prepared by thermal decomposition of Co-Fe oxalate-hydrazinate at 500 °C for 1 hour, analysed by chemical methods, Mössbauer spectrometry and electron microscopy.

Chemical analyses confirm the molar ratio Co: Fe = 1:2 in ferrite powder. The content of Co is 25.2 % and Fe 47.2 % in the obtained powder, comparable with the content of Co and Fe in $CoFe_2O_4$.

Mössbauer spectroscopy is concerned with transitions that occur inside atomic nuclei. The technique measures the resonant absorption of γ-rays by a nucleus held rigidly within a crystal.

Mössbauer data confirmed that the appearance at 500 °C a partial inverse spinelic structure appears, with the following structure: $[Co^{2+}_{0.57}Fe^{3+}_{0.43}]_{tetra}\,[Co^{2+}_{0.43}Fe^{3+}_{1.57}]_{octa}\,O^{2-}_4$.

The hyperfine parameters (e.g. isomer shift IS, quadruple splitting QS, and effective magnetic field H_{eff} as well as line width and relative weight of partial element of spectra, G, were determinated. These parameters are shown in the Table 3.

Table 3. Mössbauer data on ferrite powder obtained at 500 °C.

Coordination	IS (mm/s)	QS (mm/s)	H_{eff} (kOe)	G (%)
Fe^{3+} tetrahedral	0.24	0	484	21.6
Fe^{3+} octahedral	0.36	0	512	30.7
			496	14.8
			478	14.8
			442	14.8

The Mössbauer spectrum recorded on ferrite powder has the same shape and parameters with $CoFe_2O_4$ described on the literature. Mössbauer data confirmed that at 500 °C was obtained an inverse spinel structure. The Mössbauer parameters show that we have obtained the monophasic powder with magnetic properties.

This powder has been analysed by electronic microscopy. As shown in Fig. 4, most $CoFe_2O_4$ particles are well crystallised. The $CoFe_2O_4$ particle size fall in the size range 0.01 - 3 μm.

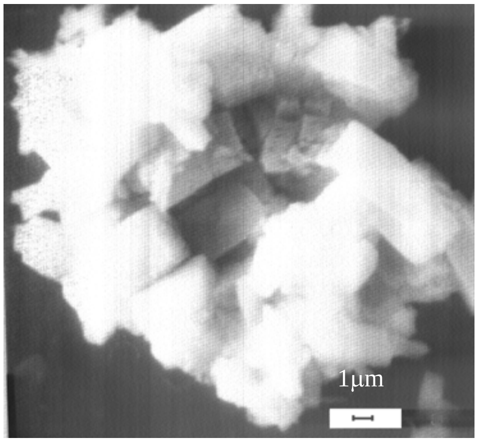

Fig. 4. The optical microscope image of cobalt ferrite.

4. Conclusions

Co-Fe oxalate hydrazinate complex with the chemical formula: $CoFe_2.3N_2H_4.6H_2O$ a very good precursor for $CoFe_2O_4$ ferrite was obtained.

The optimum composition of oxalate hydrazinate precursors from the point of view of the number of hydrazine molecules is the results of the compromise between the decomposition temperature and the violence of the decomposition. It is desired a low decomposition temperature, but also a control of the decomposition reaction is necessary. The presence of water is necessary because it is a moderator for thermal decomposition and it favours the yielding of oxide ceramics. The analyses show the presence of a crystalline compound with characteristic properties. IR spectrum of Co-Fe oxalate hydrazinate have demonstrated that hydrazine is present into complex structure.

There was demonstrated the formation of cobalt ferrite at low temperatures. Homogeneous and well crystallised ferrite powder ($CoFe_2O_4$), at 500 ^oC has been obtained.

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