SYNTHESIS OF THE SrFeO$_{2.5}$ AND BaFeO$_{3-x}$ PEROVSKITES BY THERMAL DECOMPOSITION OF SrNH$_4$[Fe(CN)$_6$] 3H$_2$O AND BaNH$_4$[Fe(CN)$_6$]

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Abstract

In the present work the synthesis, physicochemical characterization and thermoanalytical results of SrNH$_4$[Fe(CN)$_6$]3H$_2$O y BaNH$_4$[Fe(CN)$_6$] are described. The thermal decompositions in oxygen atmosphere for both salts are carried out in the stages that lead to the formation of mixed oxides, i. e., SrFeO$_{2.5}$ and BaFeO$_{3-x}$ at 1173 K. Barium carbonate is also obtained in the residue in the case of the decomposition of the barium

complex. The total weight loss are 49,95% and 35,45 % for the strontium and barium salts, respectively. A decomposition mechanism is suggested for the pyrolisis processes from the data provided by IR spectroscopy, X-ray powder diffraction and chemical analysis.

The specific surface area of the obtained oxides is also determined in order to evaluate its eventual catalytic activity.

Keywords: thermal decomposition, hexacyanoferrates(III), perovskites, thermoanalytical studies.

Resumen

En el presente trabajo se describe la síntesis, caracterización físicoquimica y resultados termoanalíticos de $SrNH_4[Fe(CN)_6]3H_2O$ y $BaNH_4[Fe(CN)_6]$. Las descomposiciones térmicas en atmósfera de oxígeno para ambas sales mixtas se lleva a cabo en tres etapas que conducen a la formación de los óxidos mixtos $SrFeO_{2.5}$ y $BaFeO_{3-x}$ a 1173 K. En el caso de la descomposición del complejo de bario se obtiene también carbonato de bario en el residuo. Las pérdidas de peso totales son del 49,95 % y del 35,45 % para la sal de estroncio y bario, respectivamente. Se propone un mecanismo de descomposición para los procesos de pirólisis a partir de la información provista por espectroscopía IR, difracción de rayos X de polvos y análisis químico.

También se determina el área superficial específica de los óxidos obtenidos para evaluar su eventual actividad catalítica.

Palabras clave: descomposición térmica, hexacianoferratos (III), perovskitas, estudios termoanalíticos.

Introduction

Nowadays the metallic oxides are the aim of many researches because they are part of important technological advances, being of particular interest those which belong to the family of the perovskites and brownmillerites. Mixed oxides with these structures are fully used in catalysis [1-11] and electrocatalysis [12-18]. ABOy perovskite type oxides ($2.5 \leq y \leq 3.0$, A=lanthanide or alkaline earth, B= transition metal) have a great technological interest due to their electrical, magnetic and catalytic properties [19]. They have been extensively used as catalyst in redox reactions, as in the reduction of nitrogen oxides and SO_2 [20, 21], hydrogenation of hydrocarbons [22], and in the elimination of atmospheric pollution [23]. In the specific case of AFeOy, iron can be in oxidation states 3+ or 4+. In the synthesis of these compounds in which iron is in an oxidation state of 4+, many oxygen vacancies are usually generated [3, 24, 25] because of the high instability of Fe(IV). In the extreme case, where y = 2.5, a brownmillerite type compound is formed with all the iron in oxidation state 3+ [2]. The mixed oxides containing Fe(III) were reported to have a good catalytic activity for NO decomposition [26]. Many properties of these oxides depend of the method of their preparation [18-21]. A way of synthesizing them is by thermal decomposition of a precursor solid which helps the homogeneity of the product and diminishes the temperature of the synthesis [1, 22].

In previous researches the mixed oxides were obtained by thermal decomposition of inorganic complexes (nitroprusside of alkaline earth metals and hexacyanoferrates of

lanthanides) in oxidative atmosphere [1-3, 27, 28]. It was shown that this method produces compounds with a high surface area, which determines the potential catalytic activity of the products [2, 3, 19].

This paper reports about the synthesis and the thermoanalytical studies of two compounds of the family of cyanometallates: ammonium and barium hexacyanoferrate(III), BaNH$_4$[Fe(CN)$_6$]; and ammonium and strontium hexacyanoferrate(III) trihydrate, SrNH$_4$[Fe(CN)$_6$].3H$_2$O whose synthesis was not reported by other authors.

The thermal decomposition of inorganic complex salts with metals in the desired range is usually a good method for producing mixed oxides at relatively low temperatures [23, 29].

In the present work we propose the synthesis of strontium and barium mixed oxides by thermal oxidative decomposition of SrNH$_4$[Fe(CN)$_6$].3H$_2$O and BaNH$_4$[Fe(CN)$_6$] in order to look for new routes of synthesis of mixed oxides. This method is simpler and more economical than those which use nitroprussides as precursors because they need a previous preparation of the silver nitroprussides [1-3].

Experimental

Synthesis

BaNH$_4$[Fe(CN)$_6$] and SrNH$_4$[Fe(CN)$_6$].3H$_2$O have been prepared for the first time by mixing stoichiometrically and stirring H$_3$[Fe(CN)$_6$], MCO$_3$ (M = Sr^{2+} or Ba^{2+}) and concentrated NH$_3$ (27 %) vigorously. The obtained precipitates were filtered and finally stored in a dry box with silica gel. The hydrogen hexacyanoferrate(III) was obtained through the technique described by Williams [30] from K$_3$[Fe(CN)$_6$]. x H$_2$O, and concentrated HCl (38%).

The preparation was carried out under a fume hood and without light due to the photochemistry of the aqueous solutions of the cianometallates. In the synthesis of BaNH$_4$[Fe(CN)$_6$] prismatic crystals [31] of hexacyanoferrates(II) and (III) were jointly obtained, and because of their size and different colour were manually separated and purified by recrystallization.

The chemical composition of the compounds was determined valueting Sr(II) through EDTA [32], Ba (II) through volumetry of precipitation with sodium rodizonate as indicator and Fe(III) through spectrofotometry (ortho-fenantroline method) [33]. The number of water molecules was calculated from the results of the TGA.

Calcd. for SrNH$_4$[Fe(CN)$_6$].3H$_2$O(%): Sr, 23.97; Fe, 15.28; NH$_4^+$, 4.93; H$_2$O, 14.78.

Found: Sr, 23.90; Fe, 15.24; NH$_4^+$, 4.82; H$_2$O, 14.92.

Calcd. for BaNH$_4$[Fe(CN)$_6$](%): Ba, 37.40; Fe, 15.21; NH$_4^+$, 4.90.

Found: Ba, 38.00; Fe, 15.45; NH$_4^+$, 4.97.

Thermal decomposition

The thermogravimetric and thermodifferential analysis (TGA and DTA) measurements were performed in a Shimadzu TGA/DTA-50 at 2 °C/min under flowing oxygen.

Based on the results of TGA, the samples were heated under oxygen flow in furnace at different temperatures during 8 hours for further studies.

Physicochemical characterization

In order to characterize the complexes and their decomposition products, IR spectroscopy, chemical analysis, and XRPD were used. IR spectra were recorded with an FTIR Perkin Elmer 1600 in the transmission mode using KBr pellets. Laboratory XRPD were performed with a PW3710 Based Diffractometer Philips with CoK_α radiation ($\lambda = 1.78896$ Å) in the range of $2\theta = 10\text{-}90$ °.

Surface areas were determined by dye adsorption method [34]. Methylene blue was used as an adsorbate. Even if dye adsorption in solution might have the problem of pore accessibility by the dye molecule, surface areas obtained in the present work correspond to those reported for nonporous materials, in which case the method has been proved to reproduce BET measurements [34].

Results and discussion

$SrNH_4[Fe(CN)_6].3H_2O$ and $BaNH_4[Fe(CN)_6]$

IR Spectra

Figures 1(a) and 2(a) show the IR spectra at room temperature for the $SrNH_4[Fe(CN)_6]. 3H_2O$ and $BaNH_4[Fe(CN)_6]$, respectively. Table 1 shows the corresponding assignations of vibrational frequencies.
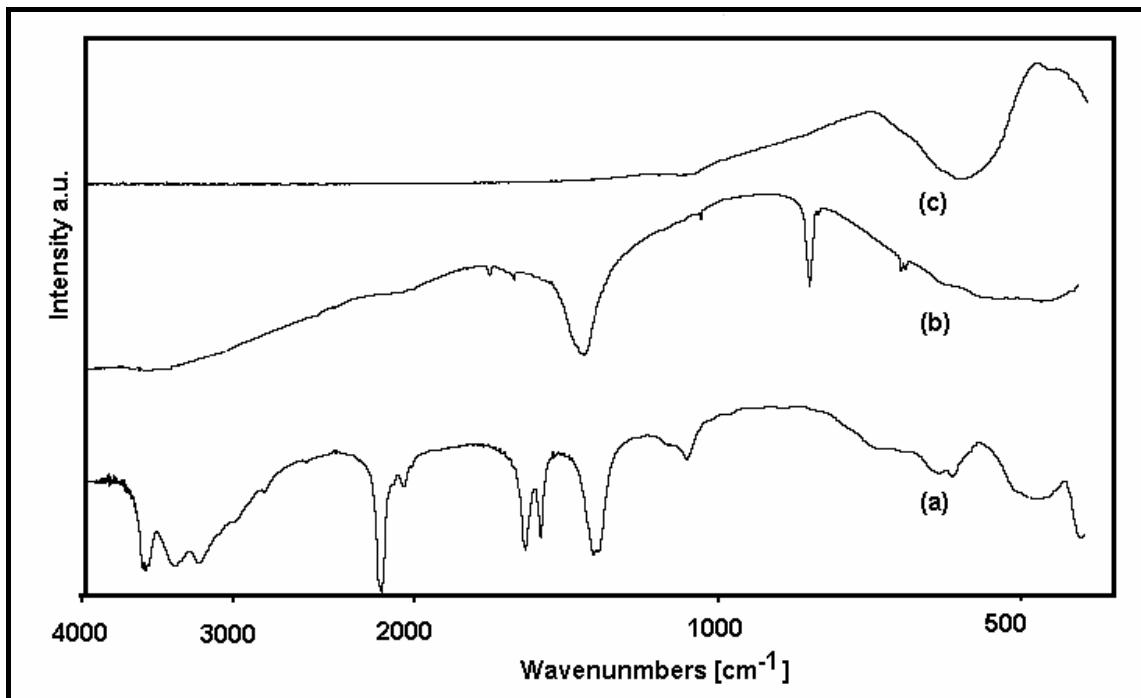

Fig.1. IR spectra for samples of $SrNH_4[Fe(CN)_6].3H_2O$ at different temperatures: a) room temperature, b) 400 °C, c) 900 °C
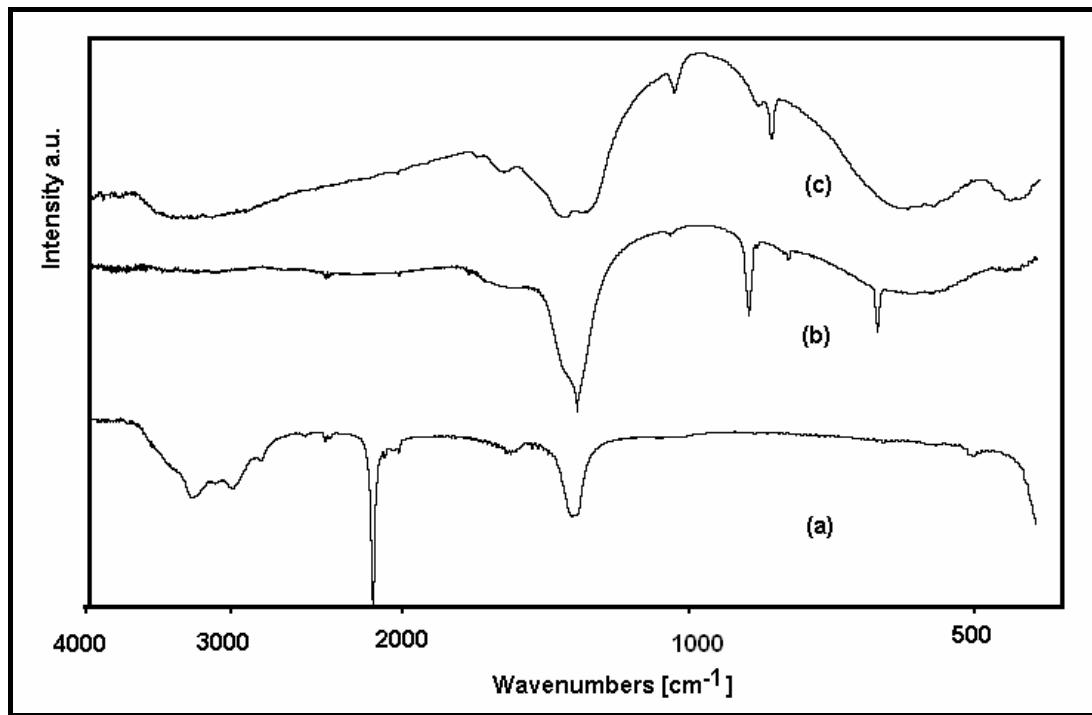
Fig.2. IR spectra of samples of BaNH$_4$[Fe(CN)$_6$] at different temperatures: a) room temperature, b) 500 ºC, c) 900 ºC.

Table 1. Assignation of FTIR spectra of SrNH$_4$[Fe(CN)$_6$].3H$_2$O and BaNH$_4$[Fe(CN)$_6$].

Assignment	Frecuencies [cm^{-1}]	
	SrNH$_4$[Fe(CN)$_6$] 3 H$_2$O	BaNH$_4$[Fe(CN)$_6$]
ν_3 H$_2$O	3632 - 3610	---------
ν_1 H$_2$O	3427	--------
ν_3 NH$_4^+$	3259	3000 - 3300
ν CN$^-$	2135	2120
ν_2 NH$_4^+$	1654	1644
ν_2 H$_2$O	1648 - 1600	-------
ν_4 NH$_4^+$	1424	1419
δ Fe-CN	600	500
ν Fe-C	450	It is not obserbed

Thermogravimetric and differential thermal analysis data

The TGA and DTA data of $SrNH_4[Fe(CN)_6].3H_2O$ are shown in Figure 3. Three steps are observed in the TGA for the thermal decomposition process in oxidative atmosphere. The total weight loss from room temperature to 900 °C is 49.95 %. Table 2 shows the decomposition mechanisms corresponding to each step.
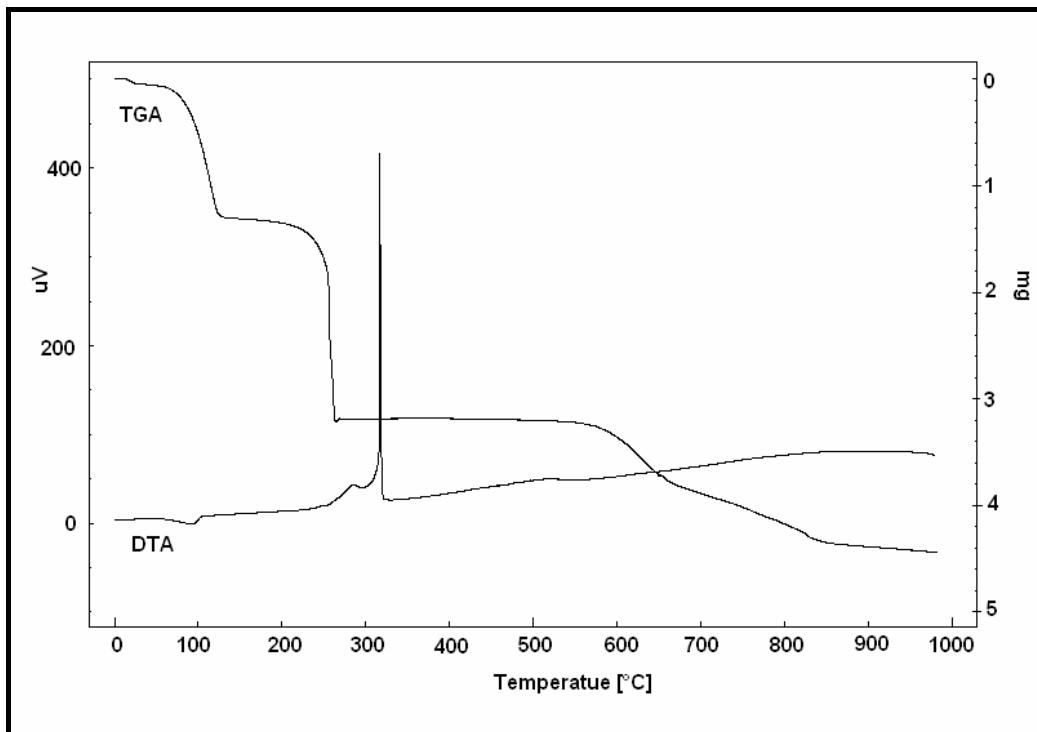

Fig.3. TGA-DTA curves of $SrNH_4[Fe(CN)_6].3H_2O$ in oxygen.

Table 2. Mechanisms proposed for the thermal decomposition in oxygen for $SrNH_4[Fe(CN)_6]. 3H_2O$.

Step	Temp. [°C]	Mechanism proposed
1	20 - 150	$SrNH_4[Fe(CN)_6] 3 H_2O_{(S)} \Rightarrow SrNH_4[Fe(CN)_6]_{(S)} + 3 H_2O_{(g)}$
2	150 - 290	$SrNH_4[Fe(CN)_6]_{(s)} + 25/4 O_{2(g)} \Rightarrow NH_4CN_{(g)} + SrCO_{3(s)} + 4 CO_{2(g)} + ½ Fe_2O_{3(s)} + 5/2 N_{2(g)}$
3	565 - 900	$½ Fe_2O_{3(s)} + SrCO_{3(s)} \Rightarrow SrFeO_{2.5(s)} + CO_{2(g)}$

The first step ends at ca. 150 °C, with weight loss of 14.92 % due to the elimination of three water molecules (theoretical value 14.78 %). This corresponds to an endothermic process observed in the DTA. The second step finishes at 290 °C in the TGA with a weight loss of 21.52 %. It can be thought that this step corresponds to the elimination of CN groups through a very exothermic process (273 ºC in DTA), with the formation of Fe$_2$O$_3$ and SrCO$_3$. The IR spectrum of the sample heated up to 400 °C (Fig. 1 (b)) confirms the presence of CO$_3^{2-}$. The third step has a weight loss of 13.51 % and corresponds to the decomposition of SrCO$_3$ and further combination with Fe$_2$O$_3$ to generate SrFeO$_{2.5}$. An endothermic pick of low energy appears in the DTA compared to the exothermic pick of the previous stage. The IR spectrum of the product at 900 ºC shows the presence of oxides (Fig. 1 (c)).

If we compare the decomposition of this complex with the one of the strontium nitroprusside, the latter produces the mixed oxides at lower temperature, 830 °C, but three succesive heatings of 12 hours are needed to obtain it free of carbonates. SrFeO$_{2.5}$ was obtained as a pure phase free of carbonates by heating only during 8 hours at 900 °C [2].

The TGA and DTA data of BaNH$_4$[Fe(CN)$_6$] are shown in Figure 4. Three main steps are observed in the TGA for the thermal decomposition process in oxidative atmosphere. The total weight loss from room temperature to 900 °C is 35,45 %. Table 3 shows the decomposition mechanisms corresponding to each step.
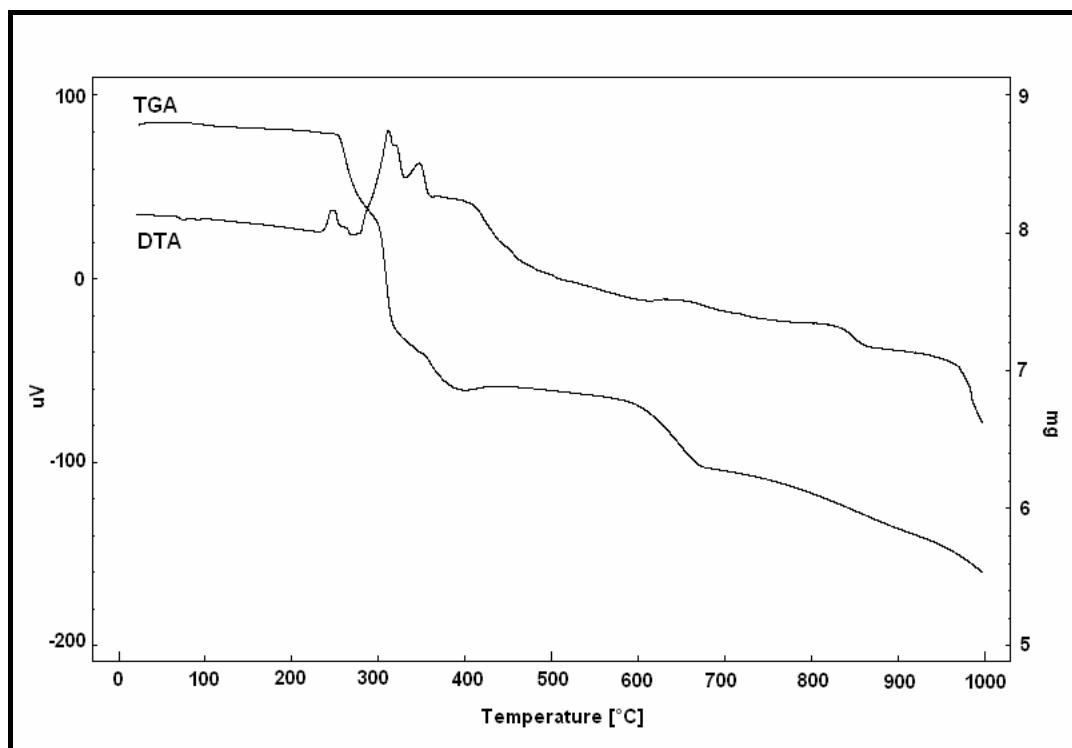

Fig.4. TGA-DTA curves of BaNH$_4$[Fe(CN)$_6$] in oxygen.

Table 3. Mechanisms proposed for the thermal decomposition in oxygen for $BaNH_4[Fe(CN)_6]$.

Step	Temp. [°C]	Mechanism proposed
1	18 - 400	$BaNH_4[Fe(CN)_6]_{(s)} + 25/4\ O_{2(g)} + \varnothing \Rightarrow \frac{1}{2}\ Fe_2O_{3(s)} + NH_4CN_{(g)} +$ $BaCO_{3(s)} + 4\ CO_{2(g)} + 5/2\ N_{2(g)}$
2	500 - 650	$BaCO_{3(s)} + \varnothing \Rightarrow BaO_{(s)} + CO_{2(g)}$ $BaO_{(s)} + \frac{1}{2}\ O_{2(g)} + \varnothing \Rightarrow BaO_{2(s)}$
3	650 - 900	$\frac{1}{2}\ Fe_2O_{3(s)} + BaO_{2(s)} + \varnothing \Rightarrow BaFeO_{3-x\ (s)} + (1/4 + x/2)\ O_{2(g)}$

Weight loss is not observed at a temperature lower than 240°C which shows that the prepared complex is anhydrous.

The first step of decomposition between 240 and 400 °C has a weight loss of 21.13 % (calculated value 20.64 %) and would correspond to the formation of $BaCO_3$ and Fe_2O_3. In the DTA three exothermic peaks are observed at: 245, 309 y 348 °C by which it is supposed that the loss of CN^- is not produced only once. The IR spectrum of the sample heated at 500 °C confirms the presence of CO_3^{2-} (Fig. 2 b).

The second step between 400 and 650 °C has a weight loss of 9,55 %. An exothermic process of little energy is observed in the DTA (at 630 ºC). It can be assumed that BaO would be initially formed in this stage and it would be oxidized to barium peroxide in oxidative atmosphere. Both processes actually occur simultaneously. The presence of BaO_2 was observed through the reaction with KI, in a diluted acid medium, which produces a blue color in the starch indicator.

For the compound of barium, the formation of barium peroxide is postulated in a stage that begins at 500 ºC, which does not happen in the case of the strontium. As reported in the bibliography, the barium peroxide formation is produced smoothly at 550 ºC, whereas the strontium oxide can only be oxidized by oxygen at high pressures at about 400 ºC. Likewise, the stability of the peroxide decreases in this order Ba: Sr: Ca, which is caused by the crowding of the peroxide ions by the smaller cations, that is reflected in the dissociation pressures at 100 ºC of 10^{-13} atm: 0.1 atm: 50 atm. Therefore, under work conditions, the formation the barium peroxide would be possible, but the formation of strontium peroxide would not be possible [35].

The third stage of decomposition starts at 650°C and ends at 900 °C and a weight loss of 4,77 % are observed which would correspond to the formation of $BaFeO_{3-x}$. Similar results were obtained by Gómez et al. for the thermal decomposition of barium nitroprusside in oxidative atmosphere [3]. An endothermic peak is observed in the DTA at 820 °C.

If the thermolysis processes of the studied complexes are compared, the process of the strontium has stages of decomposition defined and constant weight intervals between them

and the ligands CN^- are eliminated in a extremely exothermic process similar to the reported by Navarro et al. for the decomposition of neodymium hexacyanoferrate [27]. Conversely, a stage is produced in the thermolysis of the barium complex after another and the ligands do not eliminate together. Although the necessary temperature to obtain the mixed oxide is similar for both, the one of strontium is obtained pure, but, on the contrary, that of the barium is together with a small quantity of $BaCO_3$.

Decomposition products

IR spectra

The IR spectra of samples of $SrNH_4[Fe(CN)_6].3H_2O$ and $BaNH_4[Fe(CN)_6]$, heated at different temperatures, are shown in Figures 1 and 2, respectively.

For $SrNH_4[Fe(CN)_6].3H_2O$ heated to 400 ºC bands appear which correspond to $SrCO_3$ at 1454 cm^{-1} (νCO), 859 cm^{-1} ($\delta\ CO_3^{2-}$) y 700 cm^{-1} ($\delta\ OCO$) and Fe_2O_3 at 551 and 476 cm^{-1}.

There are frequencies lower than 600 cm^{-1} in the IR spectrum of the residue at 900 °C, which are typical of oxides.

For the residue of barium complex obtained at 500 °C, the IR spectrum bands indicate the presence of $BaCO_3$ at 1420 cm^{-1} (νCO), 830 cm^{-1} ($\delta\ CO_3^{2-}$), 690 cm^{-1} ($\delta\ OCO$), and broad bands of Fe_2O_3 at 584 and 460 cm^{-1} were observed. Finally, at 900 °C the bands of mixed oxide are observed at 610 and 356 cm^{-1}[36].

The treatment at 900 °C produces a sample with typical frequencies of oxides. A low level of carbonate is also detected. This is logical because of the decomposition temperature of $BaCO_3$ is 1450 ºC [37].

XRPD data

Figures 5 and 6 show the X-ray diffraction patterns for $SrNH_4[Fe(CN)_6].3H_2O$ and $BaNH_4[Fe(CN)_6]$, obtained through a heating treatment at 900 ºC. The obtained powder XRPD data were compared to the existing ones in the database Powder Diffraction File, PDF. The final product of the $SrNH_4[Fe(CN)_6].3H_2O$ would be the oxide with the formula $SrFeO_{2.5}$. The mentioned oxide belongs to the orthorhombic system with the following cell parameters: a = 5.671 Å, b = 15.59 Å and c = 5.528 Å [38].

For the $BaNH_4[Fe(CN)_6]$ the diffraction lines observed are coincident to the pattern reported by Negas Roth [39]. Consequently, it might be assumed that the final product is $BaFeO_{3-x}$, belonging to the tetragonal system with a = b = 3.985 Å, c = 4.005 Å. Some lines are also observed which correspond to the $BaCO_3$ [40].
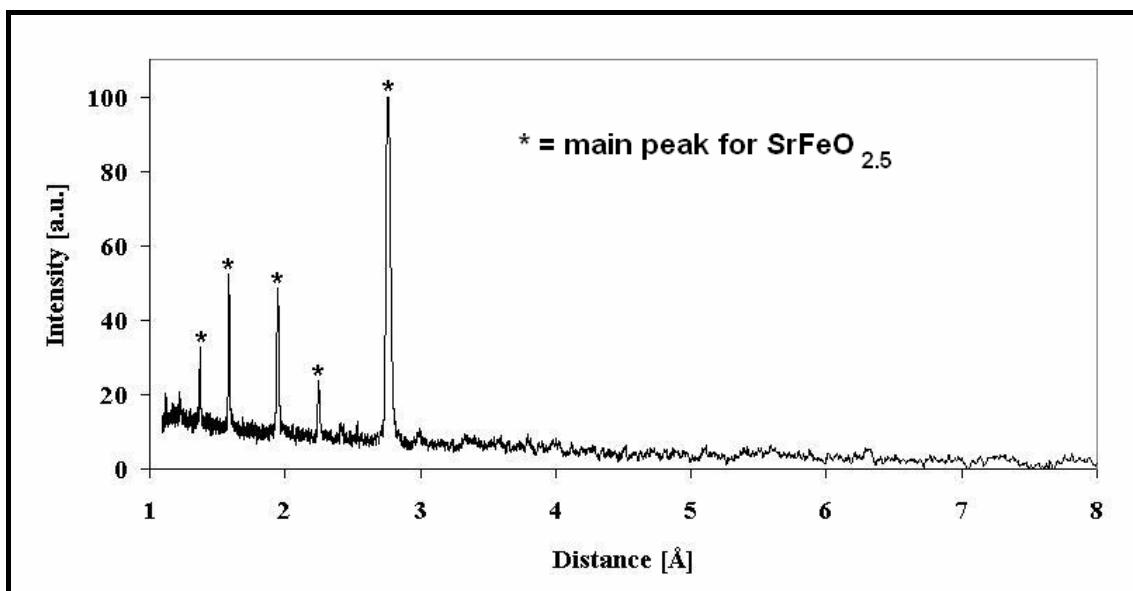
Fig. 5. X-ray powder diffraction data of the sample obtained by thermal decomposition of SrNH$_4$[Fe(CN)$_6$].3H$_2$O at 900 ºC.
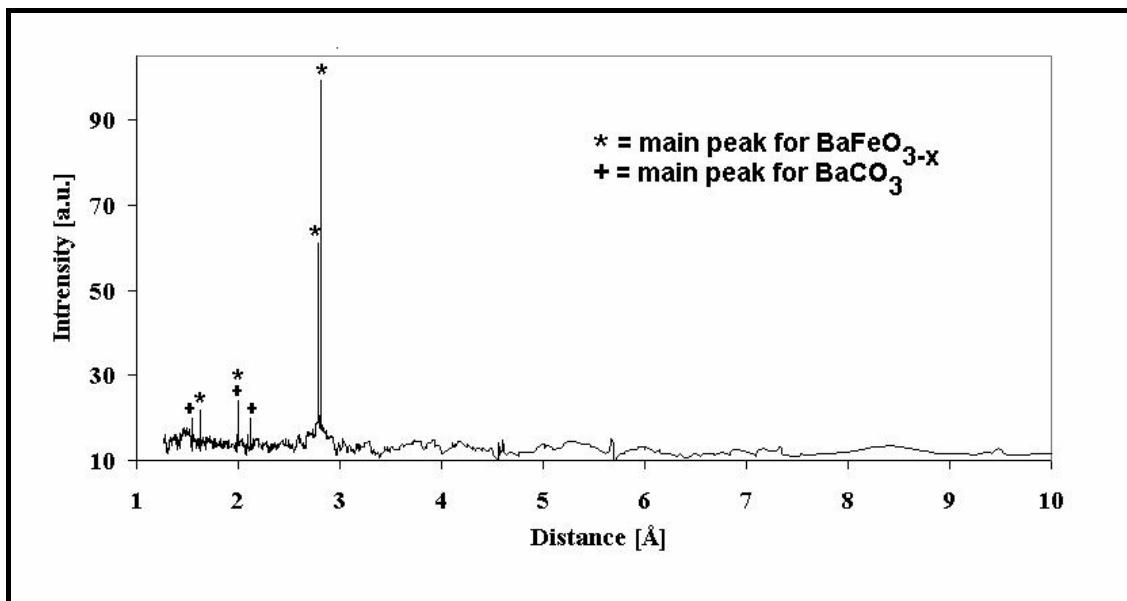

Fig. 6. X-ray powder diffraction data of the sample obtained by thermal decomposition of BaNH$_4$[Fe(CN)$_6$] at 900 ºC.

Chemical analyses and surface area of the end products

Anal. Calcd. for SrFeO$_{2.5}$ (%): Sr, 47.58; Fe, 30.44. Found: Sr, 47.51; Fe, 30.50.

Anal. Calcd. for BaFeO$_{3-x}$ (%): Ba, 58.83; Fe, 23.98. Found: Ba, 59.12; Fe, 24.10.

The surface area of SrFeO$_{2.5}$ is 1.50 m^2/g. This is a little lower to the one found for the residue of strontium nitroprusside [2] but similar to those for lanthanum perovskites obtained by calcining the mixture of lanthanum and iron oxides at 1000°C [41].

The superficial area for BaFeO$_{3-x}$ is 2.78 m^2/g . This is similar to those found for the barium nitroprusside residue [3]. These methods produce a relatively high surface area material that could have good catalytic properties [3,42-46].

Conclusions

Two metallic complexes, BaNH$_4$[Fe(CN)$_6$] and SrNH$_4$[Fe(CN)$_6$].3H$_2$O have been successfully synthesized for the first time and characterized by TGA-DTA, FTIR and XRPD techniques. The thermal decomposition under oxidative atmosphere occurs via three stages for both compounds but through different mechanisms, resulting in perovskite-type mixed oxides identified as SrFeO$_{2.5}$ and BaFeO$_{3-x}$. The process is carried out at close temperature but in a shorter time than in similar methods previously proposed. On the basis of the exposed results, the use of these complexes as precursors for the obtainment of this type of structures is very promising. The surface area of the SrFeO$_{2.5}$ and BaFeO$_{3-x}$ are similar to the obtained from other mixed oxides which indicates that they can be used with catalytic aims.

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