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Original Scientific Paper

Preparation and Characterization of Yttrium-iron Citric Acid Complexes

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Yttrium-iron(III) citric acid complexes with mole ratio Y : Fe = 1 or 3 : 5, potential precursors for $YFeO_3$ and $Y_3Fe_5O_{12}$ thin films preparation, have been synthesized in ethylene glycol medium. The compositions, IR, ^1H and ^{13}C NMR spectral characteristics of the isolated solid complexes have been studied. Their chemical nature and the peculiarities of the complexation process in the system Y^{III}–Fe^{III}–citric acid–ethylene glycol = 1 : 1 : 8.5 : 35 have been studied and compared with those of the earlier studied lanthanide(III or IV)-titanium(IV) citric acid complexes, prepared under the same conditions. The mixed-metal nature of the obtained complexes has been shown. In contrast to the analogous lanthanide-titanium system, no deprotonation of the alcoholic OH groups of citric ligands takes place in the course of the formation of Y-Fe complexes.

Key words: citric complexes, iron(III), lanthanides, titanium(IV), polymerized complex method.

INTRODUCTION

The citric precursor technique is widely used (in aqueous or ethylene glycol solutions) to produce a number of multicomponent, phase-homogeneous materials, including yttrium-iron garnet ($Y_3Fe_5O_{12}$, YIG), other $Ln_3Fe_5O_{12}$

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and $Ln_2LnFe_5O_{12}$ (Ln, lanthanide),[1,2] $NiFe_2O_4$,[3] $CoFe_2O_4$,[4] $Ln_2Ti_2O_7$,[5,6] *etc*. The authors pay attention to the precursors' composition but point to the necessity of a much better knowledge of their chemical nature.[5,6] Significant efforts have been made in the last years in this direction by studying the chemistry of the processes involved in $BaTiO_3$,[8,9] and $Ln_2Ti_2O_7$,[10–12] production in ethylene glycol (EG) medium by the polymerized complex method (PCM). However, the reasons for the citric ligands' alcoholic OH group deprotonation, taking place in the course of the complexation process in (Ba or Ln)–Ti–(CA)–EG systems (CA, citric acid) at an uncommonly low pH, have not been fully elucidated. The role of the overall charge of the complexing agents in this process was also studied by substituting Ln^{III} with Ce^{IV} in $Ln–Ti^{IV}–CA–EG$ system.[11,13] It was interesting to compare these results with the ones obtained by substituting the other complexing agent (Ti^{4+}), as a partner of Ln^{III}, with another metal ion in oxidation state III, like Fe^{3+}.

On the other side, magnetic, magneto-optical and dielectric properties of rare earth (Ln) ortoferrites and ferrite-garnetes determine their wide range of applications, including components of microwave and magneto-optic memory devices, substrate for microwave compatible YBCO high-temperature superconducting films, *etc*. A number of methods had been proposed for the preparation of these materials in polycrystalline form and of YIG thin films. $YFeO_3$ films were also produced, but by pulsed laser deposition method only.[14] To our knowledge, only one paper deals with the spray pyrolysis method as a tool for YIG film deposition using a solution of Y- and Fe-acetilacetonates.[15] We explore the possibility preparing of YIG and $YFeO_3$ films by spray pyrolysis using EG solutions of Y-Fe citric complexes as starting material, while submicron YIG films (on yttrium-aluminum garnet substrate) of a rather good quality have been already produced.[16] Such a relatively new field of application of bimetallic citrates, obtained in (and containing) EG, also requires a knowledge of their chemical nature.

In the present paper, the results are reported on the synthesis and characterization of two types of $Y\text{-}Fe^{III}$ citric complexes (potential precursors for $YFeO_3$ and YIG production), prepared in EG medium.

EXPERIMENTAL

Materials

Anhydrous citric acid (CA, extra pure), $Y(NO_3)_3 \cdot 6H_2O$ (lab), $FeCl_3$ (for synthesis) (Merck) were used. The other reagents used were of *p.a.* grade. The exact content of Y and Fe in the respective compounds was determined complexometrically.

Synthesis of the Complexes

CA was dissolved in EG at 35 °C. $Y(NO_3)_3 \cdot 6H_2O$ or/and $FeCl_3$ were added to the solution so as to enable the mole ratio $Y^{3+}(Fe^{3+}) : CA : EG = 1.0 : 4.3 : 17.6$ and $Y^{3+} : Fe^{3+} : CA : EG = 1.0 : 1.0 : 8.5 : 35.0$ or $1.00 : 1.67 : 11.30 : 46.50$ to be adjusted. The metal(s) : CA : EG ratio was analogous to the one used in the system (Y^{3+} or/and Ti^{4+})–CA–EG, applied for $Y_2Ti_2O_7$ production[5] and accounting for the difference in the oxidation states of Ti^{IV} and Fe^{III}. The obtained solutions were agitated in a thermostatically heated vessel at (110 ± 3) °C (120 °C for the monometallic Y-compound). After cooling to room temperature, acetone was added as a desalting agent in a volume 20 times as large as the one of the solution. After 24 h, the obtained precipitate was filtered, washed with acetone, dried at room temperature and stored in a tightly closed vessel. No precipitate was obtained by this procedure in the Fe^{3+}–CA–EG system though that (according to IR spectrum) a complexation process took place.

Analysis

The content of C and H in the obtained substances was determined by the common organic analysis method. The metals were determined complexometrically making use of the significant difference in the stability constants of their complexes with EDTA. The relative standard deviations of the latter procedure (derived from 4 parallel analyses of the model solution, simulating the real one) were 0.9% for Fe and 2.4% for Y. IR spectra (4000–400 cm^{-1}) were recorded by a Specord 75 (C. Zeiss, Germany) spectrometer in the capillary layer for the solutions and in nujol mulls or KBr pellets for solid substances. ^{13}C and ^{1}H NMR spectra were taken using a Bruker 250 MHz spectrometer. The amount of water was determined thermogravimetrically with a Paulik-Paulik-Erdey (MOM, Hungary) derivatograph. X-ray powder diffractometry was performed using a TUR-M62 (Germany) diffractometer at Cu-Kα, 34 kV, 15 mA, 0.05 ° / 2 s.

RESULT AND DISCUSSION

Composition and Some Spectral Characteristics of Isolated Products

The elemental composition, water content, mass loss during the heating to 1000 °C of the isolated products as well as data on the ligands' esterification and the relative content of EG, derived from NMR spectra, are shown in Table I. These data along with the ones from IR spectral analysis lead to the following formulae of the complexes:

$[Y\{HCitROH\}^{2-}\{(HCitROH)_2R\}_{0.2}^{2-}\{HCitROHRHCit\}_{0.2}^{3-}(H_2O)] \cdot 0.1HOROH \cdot \cdot 3H_2O$ (for the Y complex, labeled later in the text as Y120),[11] where $R = (CH_2)_2$, $HCit = OOCCH_2C(COO)(OH)CH_2COO$;

$[YFe(HCitHROH)_2^{-}(HCitH)_{1.5}^{2-}(HCitROH)_{0.5}^{2-}] \cdot 0.4HOROH \cdot 8H_2O$ (for the 1 : 1 Y-Fe complex, labeled as YFe110) and

$[Y_{0.6}Fe(HCitHROH)_{1.8}^{-}\,(HCitH)_{1.4}^{2-}\,(HCitROH)_{0.1}^{2-}\,(H_2O)_3]\cdot 0.5HOROH\cdot 6H_2O$ (for the 3 : 5 Y-Fe complex, labeled as 3Y5Fe110).

The coincidence between the experimentally found values for the complex composition and the calculated ones according to the above formulae is within the limits of ±5%.

A broad band with a maximum at 3350 cm^{-1} in the IR spectra (Figure 1) confirms the presence of hydrate H_2O in all of the separated complexes. The non-dissociated OH groups of citric ligands and those from their adducts with EG also contribute to the 3200–3400 cm^{-1} band intensity.

The complexation is proven by the bands of $\nu^{as}(COO^-)$ at 1595 cm^{-1} and of $\nu^{s}(COO^-)$ at 1440 and 1385 cm^{-1} (Figure 1). The band positions are the same as in the analogous Y-Ti citrate complex spectrum[11] and suggest that COO^- groups are monodentate coordinated. The slight asymmetry of the absorption maximum in Y-Fe citrate spectra, assigned to the asymmetric stretching vibration, to the lower wavenumbers shows that the bridging type of coordination may also take place. The ^{13}C NMR peak at 79.7 ppm (Figure 2) is assigned[5] to the quaternary alcoholic carbon in citrate ligands. The shift to high frequency in comparison with pure CA (≈ 75 ppm)[6] is due to the coordi-

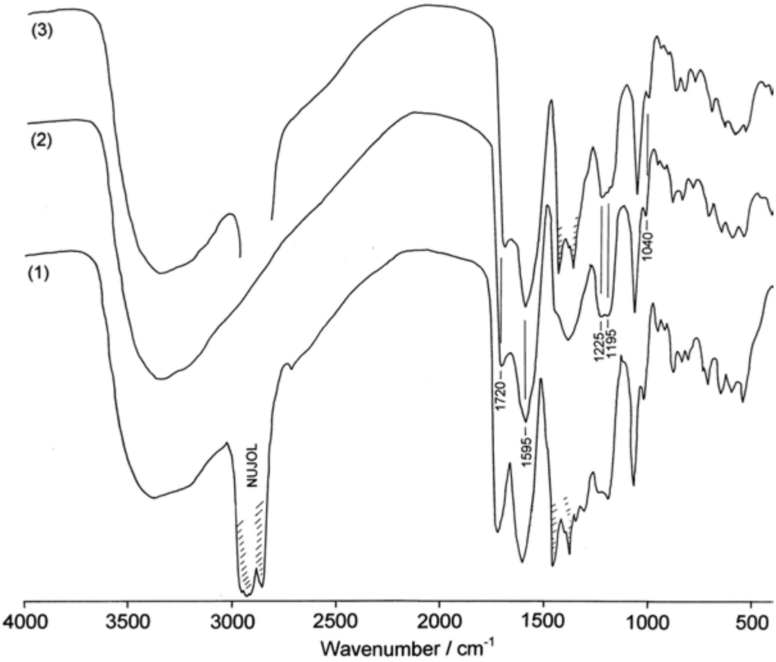

Figure 1. IR spectrum of Y-citrate (1, nujol mull) and of Y-Fe citrate with the mole ratio Y : Fe = 1 (2, KBr pellet) and Y : Fe = 3 : 5 (3, nujol mull).

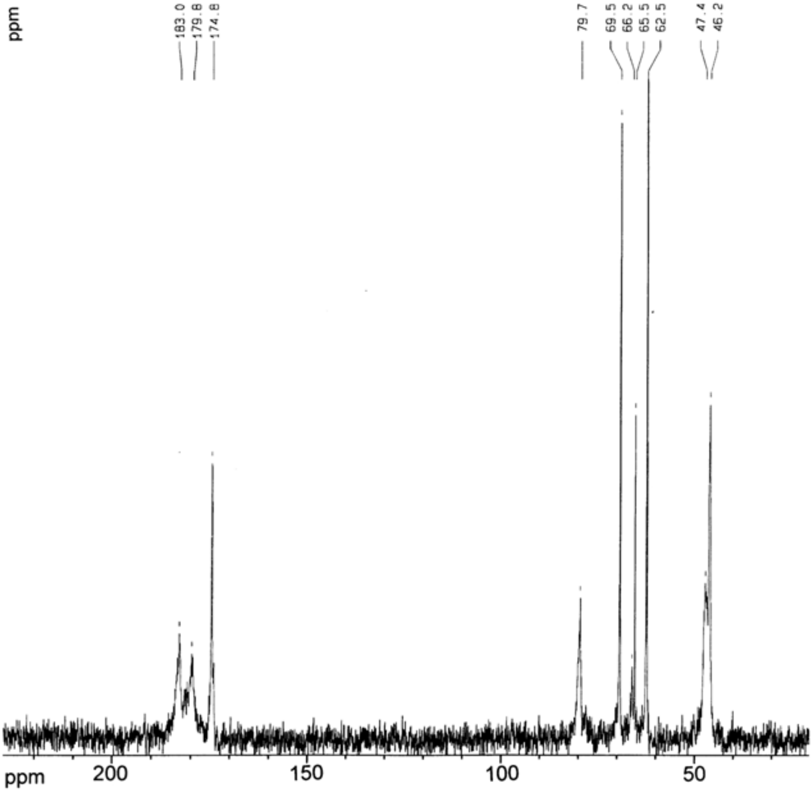

Figure 2. ^{13}C NMR spectrum of Y-Fe citrate (mole ratio Y : Fe = 1).

nation of OH to metal ions. The signal at 183.0 ppm can be attributed to the central COO^- group.[13] Formation of a five-membered ring when the OH and COO^- groups attached to the central carbon of a citrate ligand coordinate to metal ion is characteristic of Fe- and Ni citric complexes.[17,18] Considering that terminal groups of CA resonate about 176 ppm[13] and that the corresponding carboxylate anion has a shift of ≈ 5 ppm to the high frequencies,[19] we assigned the peak at 179.8 ppm to terminal COO^- groups coordinated to metal ions. The shift at 174.8 ppm can be caused by protonated and esterificated terminal carbonyl groups, whose signals are overlapped. The presence of EG, bonded as adduct, is confirmed by the IR band at 1040 cm^{-1} (Ref. 20) (Figure 1) and by the chemical shifts at 65 ppm and 3.65 ppm in the ^{13}C and ^{1}H NMR spectra,[10] respectively (Figures 2, 3).

The resonance signals at 62 and 69 ppm in ^{13}C- and 3.8 and 4.2 ppm in ^{1}H NMR spectra are associated with the CH_2 groups of esterificatied EG.[10] The peak at 4.35 ppm appears only in the Y-complex ^{1}H NMR spectrum and

TABLE I

Composition of isolated products[a]

Product symbol[b]	H	C	Y	Fe	H_2O	Residue after burning to 1000 °C[c]	Mole ratio, according to NMR data[d]		
							HOROH/Cit	ROH/Cit	R/Cit
Y120	4.37 (4.43)	29.96 (31.45)	15.30 (15.52)	– –	8.7 (9.4)	19.3 (19.7)	0.07 (0.06)	0.87 (0.88)	0.11 (0.12)
YFe110	4.00 (4.20)	29.30 (30.20)	7.25 (7.50)	4.16 (4.71)	11.0 (12.1)	15.9 (16.3)	0.10 (0.10)	0.62 (0.63)	0 (0)
3Y5Fe110	4.91 (4.98)	28.60 (29.11)	5.35 (5.25)	5.34 (5.49)	16.0 (15.9)	15.2 (14.3)	0.15 (0.15)	0.58 (0.58)	0 (0)

[a] Found (calc.) / %. Calculations based on the proposed formulae.
[b] See the text.
[c] Y_2O_3, $YFeO_3$ and YIG are taken as final products.
[d] Cit = $CH_2COOC(O)COOCH_2COO$, R = $(CH_2)_2$.

TABLE II

Some main characteristics of isolated complexes

Product symbol[a]	L[b]	Average charge of the ligands	D_{est}[c,d]		L^-/L[e]
Y120	1.80	1.67	1.03	(1.12)	0
YFe110	2.00	1.50	1.24	(1.25)	0
3Y5Fe110	2.06	1.45	0.93	(0.93)	0
YTi120[f]	1.50	2.33	2.56	(2.52)	0.6
Ce4Ti100[g]	1.50	2.67	1.96	(2.00)	1.0

[a] See the text.
[b] L = number of ligands, related to one metal ion.
[c] D_{est} = (ROH + 2R)/L, R = $(CH_2)_2$.
[d] Found (calc.); calculated according to the formulae presented in the text or in the respective papers.
[e] L^- = number of ligands with deprotonated alcoholic OH group, related to one metal ion.
[f] Y^{III}-Ti^{IV} citrate, prepared at 120 °C;[11] $[YTi\{HCitROHRHCit\}_{0.6}{}^{3-}\{CitROH\}_{1.6}{}^{3-}\{(CitROH)_2R\}_{0.1}{}^{4-}(H_2O)] \cdot 0.7HOROH \cdot 5H_2O$.
[g] Ce^{IV}-Ti^{IV} citrate, prepared at 100 °C;[13] $[CeTi(HCitROH)_{0.1}{}^{2-}(CitROH)_{2.6}{}^{3-}(H_2O)] \cdot 0.1\ HOROH \cdot 4.7\ H_2O$.

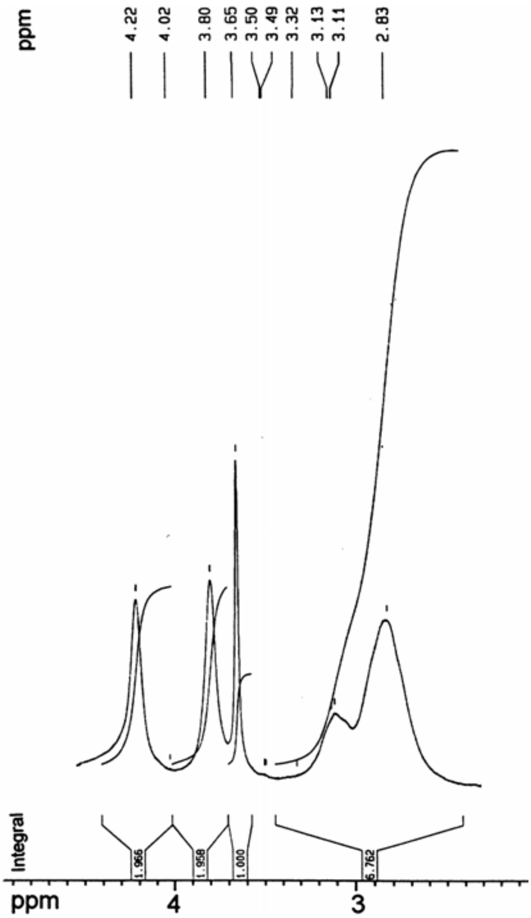

Figure 3. ^{1}H NMR spectrum of Y-Fe citrate (mole ratio Y : Fe = 1).

is caused by methylene protons of EG, bonded as ester with the central COOH group of citric ligands.[11] The intensity ratios of the cited proton signals and that of the $\mathrm{C}H_2$ in CA at 2.7–3.1 ppm allow the degree and the mode of esterification (with one or with both of the EG OH groups) to be determined (Table I). The formed esters exhibit an IR absorption maximum at 1735 cm^{-1} (ν(C=O)), strongly overlapped by the ones of the adduct (1725 cm^{-1}) and of the free COOH (1710 cm^{-1}). The band near 1200 cm^{-1} (Figure 1) is due to the C–O stretching vibration modes in the ester (1195 cm^{-1}) and in the adduct (1225 cm^{-1}).[20]

The isolated products are X-ray amorphous. The final products of their heating to 1000 °C are Y_2O_3, $YFeO_3$ and YIG, as confirmed by the mass loss (Table I) and X-ray powder diffractometry.

Chemical Nature of the Yttrium-iron Citrates

One of the main questions arising is whether a mixed-metal complex or a mixture of unimetallic complexes is formed. The problem has been already discussed in the literature considering the analogous systems precursors of a number of high-quality materials produced by the PCM. The comparative study carried out for the respective monometallic and bimetallic Y-Ti citrate compounds[11] shows, fairly definitely, the mixed-metal nature of the latter.

Due to our failure to obtain a solid Fe citrate, comparison could be made only between Y- and Y-Fe complexes. At the same time, this failure is the evidence, although not fully undoubtedly, that the bimetallic precipitate could not be a mixture of complexes. A few other facts support this supposition: (i) the shift at 4.35 ppm observed in the Y-complex ^{1}H NMR spectrum does not exist in the bimetallic complex spectrum; (ii) the ratio of the 3.8 and 4.2 ppm signal intensities clearly shows that the bimetallic product EG does not form esters through both of its OH groups simultaneously. This type of esterification is found[11] in Y complexes (Table I), even in that prepared at 40 °C; (iii) the thermal decomposition of the Y- and Y-Fe citrate complexes proceeds in different ways.[21]

Along with the obvious analogy between Y-Ti and 1:1 Y-Fe citrates, there are two significant differences: in the number of ligands and in the lack of ligands with deprotonated alcoholic OH groups in Y-Fe complexes. In contrast to analogous Y-Ti,[11] Ce^{IV}-Ti,[13] La-Ti[10] citric complexes, no ^{13}C resonance signal of quaternary carbon in CA with dissociated alcoholic OH group exist in the NMR spectrum (Figure 2). (In the earlier studied complexes the cited signal appeared at 91 ppm). Therefore, the statement[5] that the deprotonation of the alcoholic OH group proceeds only in the formation of a mixed-metal citric complex cannot be related to Ti-free systems. Furthermore, it was shown[11] that the alcoholic OH deprotonation could take place in the course of the monometallic complex formation, as well. Thus, it seems that the above mentioned statement[5] has to be ignored. The present results fully correspond to the concept[11] that the OH deprotonation is one of the few competitive processes that take place in the course of complexation, including also adduct formation, esterification and complexation through deprotonated COOH groups. Balance between these processes depends on the nature of the complexing agent(s) (oxidation state, *i.e.* overall charge, catalytic activity on the esterification), temperature of the synthesis, nature of the ligands and the limitations introduced by the steric factor. All of the results obtained to date[10,11,13] support the supposition that the OH deprotonation may become an energetically advantageous process when a high degree of esterification creates an insufficiency of COOH groups available for coordination and this insufficiency cannot be avoided by the increase of the ligand number. The increase of the overall charge of the complexing agents in Ce^{IV}-Ti^{IV} complex, compared to the Ln^{III}-Ti^{IV} ones, causes a sharp increase of the relative content of ligands with a deprotonated OH group (Table II). In contrast, the rather low degree of esterification in Y-Fe citrates, along with the higher ligand number than in the analogous Y-Ti citrates, makes a deprotonation of OH groups unnecessary – more than enough COOH groups are available for coordination. The higher ligand number in Y-Fe citrates could be due to their smaller effective size, as a result of the lower esterification degree.

The fact that the alcoholic OH group deprotonation is observed (so far, at least) in Ti^{IV}-containing systems only, suggests a possible catalytic function, especially of Ti^{4+} ions in this process. However, the deprotonation was not observed in the Y^{III}–Ti^{IV}–CA–EG system heated at 40 °C.[11] Even if the deprotonated OH groups also exist as traces in the thus obtained product, it is clear that such a catalytic effect could not be the sole reason for the discussed deprotonation.

CONCLUSION

The reported data suggest that mixed Y^{III}-Fe^{III} citrates are formed at 100 °C in the Y^{3+}–Fe^{3+}–CA–EG systems but their composition and the way of bonding are different from those of the analogous Y^{III}-Ti^{IV} bimetallic citric complexes, prepared under similar conditions. The reported results contribute to further elucidation of the chemistry of the processes taking place in the application of the polymerized complex method and especially of the mechanism of deprotonation of the citric ligands alcoholic OH group.

The Y : Fe mole ratios in the prepared complexes are rather close to the desired ones and, from this point of view, they are suitable starting materials for $YFeO_3$ and YIG film depositions.

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SAŽETAK

Priprava i karakterizacija kompleksa itrija i željeza s limunskom kiselinom

Dimitr S. Todorovsky, Desislava G. Dumanova, Rumiana V. Todorovska i Miroslava M. Getsova

Pripravljeni su kompleksi itrija i željeza(III) s limunskom kiselinom u etilen-glikolnom mediju, kao mogućih preteča za pripravu $YFeO_3$ i $Y_3Fe_5O_{12}$ tankih filmova. Kompleksi su ispitani IR te ^1H i ^{13}C NMR spektroskopijom. Rezultati dobiveni za sustav Y^{III}–Fe^{III}–citronska kiselina–etilen glikol = 1 : 1 : 8.5 : 35 uspoređeni su s ranije dobivenim rezultatima za mješovite komplekse lantanoida(III i IV) i titanija(IV) s limunskom kiselinom, koji su pripravljeni pod istim uvjetima. Za razliku od kompleksa lantanoida i titanija, pri stvaranju kompleksa itrija i željeza ne dolazi do deprotoniranja alkoholne OH skupine u ligandu.