

# THERMAL ANALYSIS OF SOME POLYNUCLEAR COORDINATION COMPOUNDS

## Ligand tartarate, precursors of $\text{LnFeO}_3$ perovskites

L. Patron<sup>1</sup>, P. Budrugaec<sup>2</sup>, A. Balu<sup>1</sup>, Oana Carp<sup>1\*</sup>, L. Diamandescu<sup>3</sup> and M. Feder<sup>3</sup>

<sup>1</sup>Institute of Physical Chemistry, ‘I. Murgulescu’, Splaiul Independentei, No. 202, 060021 Bucharest, Romania

<sup>2</sup>ICPE-CA, Research and Development Institute, 313 Splaiul Unirii, Sector 3, Bucharest, Romania

<sup>3</sup>National Institute of Materials Physics, P. O. Box MG-7, Bucharest, Romania

The thermal behaviour of five polynuclear coordination compounds containing tartaric anion as ligand, namely  $(\text{NH}_4)_3[\text{LnFe}(\text{C}_4\text{O}_6\text{H}_4)_3(\text{OH})_3]$  ( $\text{Ln}=\text{La}$  and  $\text{Eu}$ ),  $(\text{NH}_4)_2[\text{PrFe}(\text{C}_4\text{O}_6\text{H}_4)_3(\text{OH})_2]$  and  $(\text{NH}_4)[\text{LnFe}(\text{C}_4\text{O}_6\text{H}_4)_3(\text{OH})]\cdot 3\text{H}_2\text{O}$  ( $\text{Ln}=\text{Nd}$  and  $\text{Gd}$ ) was investigated. The reaction progress was studied by TG/DTA and FTIR measurements. Oxalates and oxocarbonates were identified as intermediates. In the case of  $\text{Ln}=\text{La}$ ,  $\text{Nd}$ ,  $\text{Pr}$ ,  $\text{Eu}$  and  $\text{Gd}$ , pure  $\text{LnFeO}_3$  was obtained as final decomposition product. The thermal decomposition of  $\text{Eu-Fe}$  compound, leads to a mixture of mixed (ortho-ferrite ( $\text{EuFeO}_3$ ) and garnet ( $\text{Eu}_3\text{Fe}_5\text{O}_{12}$ )) and simple oxides ( $\text{Eu}_2\text{O}_3$  and  $\alpha\text{-Fe}_2\text{O}_3$ ).

**Keywords:** lanthanide-iron coordination compound, ortho-ferrite, thermal analysis

### Introduction

It is well-known that the synthesis procedures play an important role in materials characteristics. The preparation of mixed oxides, including perovskites ( $\text{LnMeO}_3$ ,  $M=\text{Mn}$ ,  $\text{Fe}$ ,  $\text{Cr}$ ) through thermal decomposition of coordination compounds precursors leads to high homogeneity and low particle sizes of the final mixed oxides [1]. In the last decades, the investigations directed to the thermal decomposition of coordination compounds proved to be a major interest due to their use for controlled synthesis of simple and mixed oxides [2, 3].

The synthesis of  $\text{LnMeO}_3$  oxides by thermal decomposition of heteronuclear complexes was first proposed by Gallagher [3] in 1968 who used ferri- and cobaltcyanide  $\text{La}[\text{Me}(\text{CN})_6]\cdot n\text{H}_2\text{O}$  ( $M=\text{Fe}$  or  $\text{Co}$ ), as precursors. Cyanides complexes precursors were used also to obtain bi- and trimetallic perovskite-type oxides [1, 5–9]. Another class of coordination compounds precursors is represented by the double complex  $[\text{Co}(\text{NH}_3)_6][\text{La}(\text{CO}_3)_3]\cdot \text{H}_2\text{O}$  synthesized by Sakamoto *et al.* [8]. Polyhydroxycarboxylates polynuclear compounds such as malates, tartarates and gluconates compounds were used in synthesis of some manganites [9, 10], cobaltites [13] and chromites [14] by Patron *et al.*

The aim of the present study is to investigate the thermal behaviour of some iron-rare earth tartarates with molecular formulas  $(\text{NH}_4)_3[\text{LnFe}(\text{C}_4\text{O}_6\text{H}_4)_3(\text{OH})_3]$

(where  $\text{Ln}=\text{La}$  and  $\text{Eu}$ ),  $(\text{NH}_4)_2[\text{PrFe}(\text{C}_4\text{O}_6\text{H}_4)_3(\text{OH})_2]$  and  $(\text{NH}_4)[\text{LnFe}(\text{C}_4\text{O}_6\text{H}_4)_3(\text{OH})]\cdot 3\text{H}_2\text{O}$  (where  $\text{Ln}=\text{Nd}$  and  $\text{Gd}$ ), in order to determine their suitability as precursors for  $\text{LnFeO}_3$  synthesis.

### Experimental

As raw materials in precursors synthesis,  $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ ,  $\text{Ln}(\text{NO}_3)_3\cdot n\text{H}_2\text{O}$  ( $\text{Ln}=\text{La}$ ,  $\text{Nd}$ ,  $\text{Pr}$ ,  $\text{Eu}$  and  $\text{Gd}$ ) and tartaric acid ( $\text{HOOC}-(\text{CHOH})_2-\text{COOH}$ ) of reagent quality, in a molar ratio  $\text{Ln}^{3+}-\text{Fe}^{3+}-\text{tartaric acid} = 1:1:3$  were used. The iron-lanthanides complexes ( $\text{Ln}=\text{La}$ ,  $\text{Nd}$ ,  $\text{Pr}$ ,  $\text{Gd}$  and  $\text{Eu}$ ) were separated from the reaction medium (solutions containing  $\text{Ln}^{3+}-\text{Fe}^{3+}-\text{tartaric acid}$ ) by extraction with ethanol. For a complete precipitation, 24 h was necessary together with repeated adjustment of the pH to  $\sim 5$  with an ethanolic solution of ammonia. The precipitates were filtered, washed with ethanol, and dried on  $\text{P}_4\text{O}_{10}$  in vacuum. The obtained precipitates characterized by  $(\text{NH}_4)_3[\text{LnFe}(\text{C}_4\text{O}_6\text{H}_4)_3(\text{OH})_3]$  (where  $\text{Ln}=\text{La}$  and  $\text{Eu}$ ),  $(\text{NH}_4)_2[\text{PrFe}(\text{C}_4\text{O}_6\text{H}_4)_3(\text{OH})_2]$  and  $(\text{NH}_4)[\text{LnFe}(\text{C}_4\text{O}_6\text{H}_4)_3(\text{OH})]\cdot 3\text{H}_2\text{O}$  (where  $\text{Ln}=\text{Nd}$  and  $\text{Gd}$ ) formulas, are yellow coloured, water-soluble and insoluble in most organic solvents.

The coordination compounds were identified by quantitative analysis. The iron content was determined by a spectrometric technique, the lanthanide

\* Author for correspondence: carp@acodarom.ro

content by a gravimetric method and, the carbon, nitrogen and hydrogen contents by a combustion method on a Carlo Erba Model 1108-CHNS-O elemental analyser.  $\text{LaFeC}_{12}\text{H}_{27}\text{N}_3\text{O}_{21}$ : found (%) / calculated (%) La, 18.69/18.67; Fe, 7.40/7.50; C, 19.38/19.36; H, 3.63/3.63; N, 5.65/5.64.

$\text{NdFeC}_{12}\text{H}_{23}\text{NO}_{22}$ : found (%) / calculated (%) Nd, 19.69/19.67; Fe, 7.51/7.61; C, 19.66/19.64; H, 3.14/3.13; N, 1.91/1.90.

$\text{PrFeC}_{12}\text{H}_{22}\text{N}_2\text{O}_{20}$ : found (%) / calculated (%) Pr, 19.48/19.82; Fe, 7.75/7.85; C, 20.28/20.26; H, 3.09/3.09; N, 3.94/3.93.

$\text{EuFeC}_{12}\text{H}_{23}\text{N}_3\text{O}_{21}$ : found (%) / calculated (%) Eu, 20.10/20.07; Fe, 7.28/7.37; C, 19.04/19.02; H, 3.57/3.56; N, 5.55/5.54.

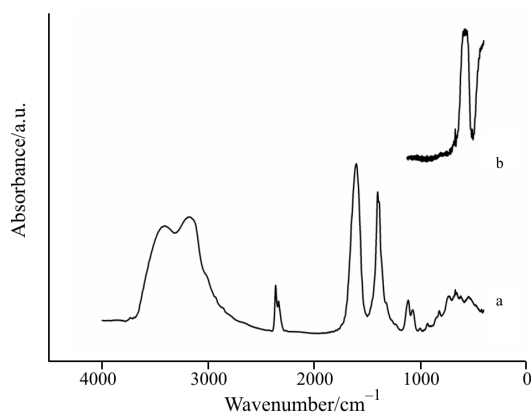
$\text{GdFeC}_{12}\text{H}_{23}\text{NO}_{22}$ : found (%) / calculated (%) Gd, 21.09/21.07; Fe, 7.38/7.48; C, 19.32/19.30; H, 3.08/3.08; N, 1.87/1.87.

The thermal measurements (TG, DTG, DTA) were performed using a Q-1500 D Paulik-Paulik-Erdey derivatograph in a static air atmosphere, at heating rates in the Fig. 2, with sample mass of ~40 mg, in ceramic crucibles with  $\alpha\text{-Al}_2\text{O}_3$  as reference compound. FTIR spectra (400-4000  $\text{cm}^{-1}$ ) were recorded with a BIO-RAD FTIR 125 type spectrophotometer in KBr pellets. The structure of the as-synthesized powders was examined with a DRON X-ray powder diffractometer linked to a data acquisition and processing facility.  $\text{CuK}_\alpha$  radiation ( $\lambda=1.540598\text{\AA}$ ) and a graphite monochromator have been used.

## Results and discussion

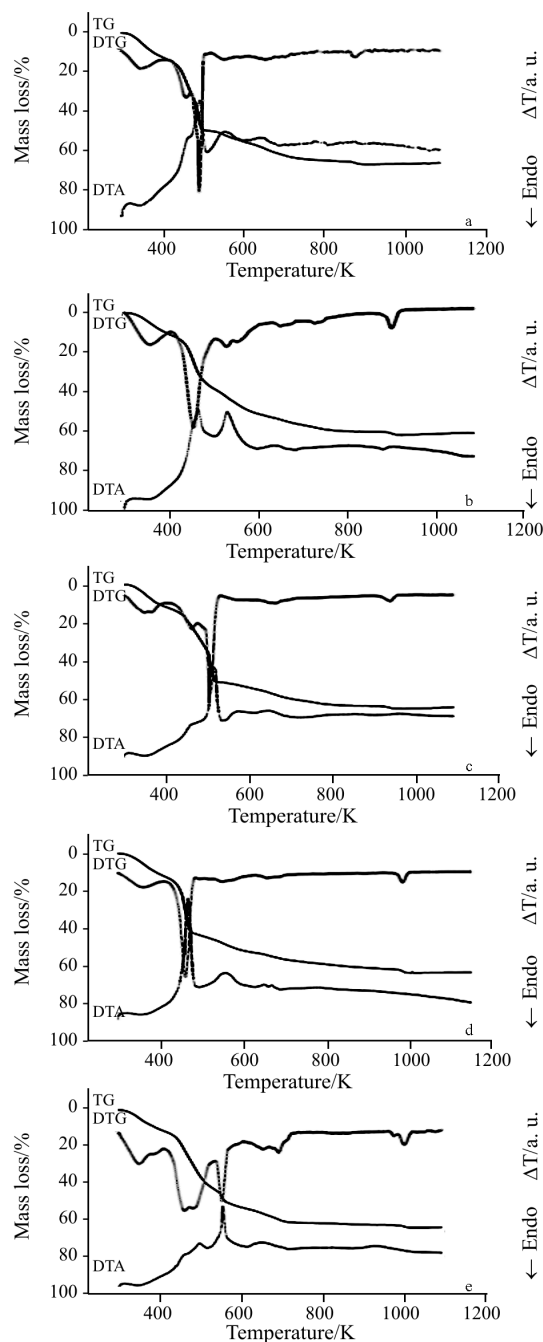
### Characterization of the coordination compounds

The corresponding IR spectra of the five coordination compounds suggest a similar coordination of the tartarate anion, namely coordination to the metal ions



**Fig. 1** IR spectra of the polynuclear compound a -  $(\text{NH}_4)_2[\text{PrFe}(\text{C}_4\text{O}_6\text{H}_4)_3(\text{OH})_2]$  and b - the corresponding oxide,  $\text{PrFeO}_3$  obtained after a thermal treatment of 1 h at 1073 K

through both its two  $\text{COO}^-$  and  $\text{C-OH}$  groups. This statement is supported by the split of the free carboxylic group band ( $\sim 1746\text{ cm}^{-1}$ ) into two very strong bands characteristic for coordination carboxylic group ( $\nu_{\text{COOasym}} \sim 1600\text{ cm}^{-1}$  and  $\nu_{\text{COOsym}} \sim 1400\text{ cm}^{-1}$ ), and by the split of the band assigned to  $\nu_{\text{C-OH}}$  ( $\sim 1088\text{ cm}^{-1} \rightarrow 1110\text{-}1060\text{ cm}^{-1}$ ). The splitting of



**Fig. 2** TG, DTG and DTA curves of the: a -  $(\text{NH}_4)_3[\text{LaFeC}_4\text{O}_6\text{H}_4)_3(\text{OH})_3]$ ; b -  $(\text{NH}_4)_2[\text{PrFe}(\text{C}_4\text{O}_6\text{H}_4)_3(\text{OH})_2]$ ; c -  $(\text{NH}_4)[\text{NdFe}(\text{C}_4\text{O}_6\text{H}_4)_3(\text{OH})] \cdot 3\text{H}_2\text{O}$ ; d -  $(\text{NH}_4)_3[\text{EuFe}(\text{C}_4\text{O}_6\text{H}_4)_3(\text{OH})_3]$ ; e -  $(\text{NH}_4)[\text{GdFe}(\text{C}_4\text{O}_6\text{H}_4)_3(\text{OH})] \cdot 3\text{H}_2\text{O}$

$\nu_{\text{OCOasym}}$  and  $\nu_{\text{OCOSym}}$  vibrations leads to values of the magnitude of separation  $\Delta\nu$  ( $\Delta\nu = \nu_{\text{OCOasym}} - \nu_{\text{OCOSym}}$ ) of  $\sim 200 \text{ cm}^{-1}$ , typical for unidentate coordination of  $\text{COO}^-$  groups [15]. The presence of the doublet at  $1110\text{--}1060 \text{ cm}^{-1}$  means a dissimilar coordination of the two C–OH groups to two different metallic cations ( $\text{Ln}^{3+}$  and  $\text{Fe}^{3+}$ ) [14, 16, 17]. The bands appearing at in the range  $500\text{--}650 \text{ cm}^{-1}$ , can be attributed to M–O stretching vibration. To exemplify this affirmation the IR spectra of  $(\text{NH}_4)_2[\text{PrFe}(\text{C}_4\text{O}_6\text{H}_4)_3(\text{OH})_2]$  is presented in Fig. 1a.

#### Non-isothermal analysis of the polynuclear compounds

The thermal curves (TG, DTG and DTA) of the five polynuclear coordination compounds are displayed in Fig. 2 a–e. The thermal decomposition data on the coordination compounds are listed in Table 1.

Several common characteristics may be pointed out:

- the thermal behaviour of the investigated compounds occurs in six decomposition steps in the temperature range  $309.7\text{--}1018.0 \text{ K}$ ;
- the observed mass losses, (65.70% (La), 65.43% (Nd), 64.42% (Pr), 63.81% (Eu) and 64.00% (Gd)) confirm the formation of compounds with molecular formula  $\text{LnFeO}_3$  as end decomposition products, (theoretical mass losses: 67.43% (La), 66.23% (Nd), 65.63% (Pr), 66.26% (Eu) and 65.07% (Gd)). The lower values of registered mass losses (ranging from 0.8 to 2.45%) are determined by the adsorption on the surface of organic residue (resulted during decomposition). Their presence is confirmed by the IR bands identified in the range  $1700\text{--}850 \text{ cm}^{-1}$ . An extended thermal treatment leads to pure oxide(s), the above mentioned bands being not any more detected in IR spectra;
- the first decomposition stage which occurs in the temperature range  $309.7\text{--}411.6 \text{ K}$  is associated with an endothermic effect. It represents the evolving of ammonia and water. In the case of the compounds which contain crystallization water (Nd–Fe and Gd–Fe compounds) two maxima are identified on DTG curve, the one which appear at higher tem-

peratures ( $\sim 363 \text{ K}$ ) corresponding to water elimination. The initial ( $T_{i1}$ ), final ( $T_{f1}$ ) and maximum DTG temperature ( $T_{\text{max}1 \text{ DTG}}$ , the temperature at which the decomposition rate is maximum) of this decomposition step, do not vary gradually with the atomic number  $Z$  of the lanthanide ions;

- the second decomposition step corresponds to the transformation of tartarate anions to oxalates and further to carbonates. For La–Fe and Nd–Fe compounds, the decomposition stage occurs up to  $\sim 473 \text{ K}$  and the conversion is only partial, leading to  $[\text{LnFe}(\text{tart})_3(\text{ox})_2]$  intermediates. In the case of the other compounds, the decomposition step is completed at higher temperatures (up to  $\sim 533 \text{ K}$ ) and  $[\text{PrFe}(\text{ox})_2(\text{CO}_3)]$  and  $[\text{LnFe}(\text{ox})(\text{CO}_3)_2]$  ( $\text{Ln} = \text{Eu}$  and  $\text{Gd}$ ) formation is favoured. The IR analysis of the decomposition intermediates supports the above mechanism. The disappearance with increasing temperature of the bands assigned to  $\nu_{\text{C-OH}}$  ( $\sim 1110$  and  $1060 \text{ cm}^{-1}$ ) and  $\nu_{\text{C-H}}$  ( $\sim 900 \text{ cm}^{-1}$ ) characteristic for the presence of tartarate anions as ligands and, the conservation of the bands specific for carboxylate anion ( $\sim 1600$  and  $\sim 1400 \text{ cm}^{-1}$ ) indicates the formation of oxalate. The carbonate existence is confirmed by the presence of the strong absorption bands at  $\sim 1500$  and  $\sim 1420 \text{ cm}^{-1}$  and the weak bands at  $\sim 1070$  and  $\sim 840 \text{ cm}^{-1}$ ;
- the second step intermediates are unstable being converted at further heating into oxocarbonates.  $\text{LnFe}(\text{CO}_3)_{2.5}\text{O}_{0.5}$  ( $\text{Ln} = \text{La}$  and  $\text{Nd}$ ) are obtained when the final decomposition temperature of the step is  $\sim 523 \text{ K}$  and  $\text{LnFe}(\text{CO}_3)_2\text{O}$  ( $\text{Ln} = \text{Pr}$ ,  $\text{Eu}$  and  $\text{Gd}$ ) when the final temperature is  $593\text{--}623 \text{ K}$ ;
- the oxocarbonates undergo a further three steps decomposition, being converted into oxocarbonates with lower content of carbonate and finally to oxides.  $\text{LnFe}(\text{CO}_3)_{0.25}\text{O}_{0.75}$  intermediates are identified for all five coordination compounds as intermediates in the last but one decomposition step;
- the last decomposition step represents the formation of the oxides corresponding to molecular formula of  $\text{LnFeO}_3$ . A lower ionic radius of lanthanide ions determines a decrease of the temperature at which the rate is maximum ( $T_{\text{max}6 \text{ DTG}}$ ) and of the final one ( $T_{f6}$ ):

Lanthanide	$\text{La}^{3+}$	$\text{Pr}^{3+}$	$\text{Nd}^{3+}$	$\text{Eu}^{3+}$	$\text{Gd}^{3+}$
Ion radius/nm [18]*	0.1061	0.1013	0.0995	0.0950	0.0938
$T_{\text{max}6 \text{ DTG}}/\text{K}$	872.7	901.0	938.0	980.0	999.0
$T_{f6}/\text{K}$	900.7	917.0	960.4	1009.6	1018.0

\*ionic radius value assuming a coordination number equal with 6

**Table 1** Thermal decomposition data of the Ln–Fe ( $Ln=La, Nd, Pr, Eu$  and  $Gd$ ) polynuclear coordination compounds

Compound	Stage	$T_i-T_f/$	$T_{max\ DTG}/$	Mass loss/%		Intermediate
		K	K	exp.	theor.	
$(NH_4)_3[LaFe(tart^*)_3(OH)_3]$	1	314.0–411.6	343.5	13.74	14.13	$[LaFe(tart)_3]$
	2	411.6–464.3	455.7	15.34	16.15	$[LaFe(tart)(ox^*)_2]$
	3	464.3–496.4	486.9	21.20	22.34	$[LaFe(CO_3)_{2.5}O_{0.5}]$
	4	496.4–617.4	550.2	5.94	5.92	$[LaFe(CO_3)_{1.5}O_{1.5}]$
	5	496.4–762.8	651.0	7.87	7.4	$[LaFe(CO_3)_{0.25}O_{0.75}]$
	6	852.9–900.7	872.7	1.61	1.48	$LaFeO_3$
$(NH_4)_2[PrFe(tart)_3(OH)_2]$	1	312.5–401.3	356.0	10.11	9.85	$[PrFe(tart)_3]$
	2	401.3–502.9	454.2	29.8	29.29	$[PrFe(ox)_2(CO_3)]$
	3	502.9–593.0	528.6	12.8	14.04	$PrFe(CO_3)_2O$
	4	593.0–707.8	651.4	7.15	7.73	$PrFe(CO_3)_{0.75}O_{2.25}$
	5	593.0–822.6	727.4	3.00	3.09	$PrFe(CO_3)_{0.25}O_{2.75}$
	6	870.2–917.0	901.0	1.54	1.63	$PrFeO_3$
$(NH_4)_2[NdFe(tart)_3(OH)] \cdot 3H_2O$	1	310.0–397.8	349.0, 365.0	12.15	11.45	$[NdFe(tart)_3(OH)]$
	2	397.8–472.0	460.0	16.11	16.58	$[NdFe(tart)(ox)_2]$
	3	472.0–527.0	509.4	22.56	23.20	$NdFe(CO_3)_{2.5}O_{0.5}$
	4	527.0–650.0	~572	4.78	6.00	$NdFe(CO_3)_{1.5}O_{1.5}$
	5	658.0–827.5	657.0	8.12	7.51	$NdFe(CO_3)_{0.25}O_{0.75}$
	6	909.2–960.4	938.0	1.71	1.50	$NdFeO_3$
$(NH_4)_3[EuFe(tart)_3(OH)_3]$	1	309.7–410.4	355.1	13.14	14.00	$[EuFe(tart)_3]$
	2	527.0–474.1	458.2	30.27	30.94	$[EuFe(ox)(CO_3)_2]$
	3	474.1–625.1	577.0	9.71	9.60	$EuFe(CO_3)_2O$
	4	625.1–753.7	638.7	5.02	5.86	$EuFe(CO_3)O_2$
	5	753.7–960.4		4.03	4.40	$EuFe(CO_3)_{0.25}O_{0.75}$
	6	753.7–1009.6	980.0	1.64	1.46	$EuFeO_3$
$(NH_4)[GdFe(tart)_3(OH)] \cdot 3H_2O$	1	311.07–411.5	347.6, 366.0	11.71	11.94	$[GdFe(tart)_3(OH)]$
	2	753.7–533.3	459.6 482.6	31.61	31.68	$[GdFe(ox)(CO_3)_2]$
	3	533.3–604.6	551.9	9.77	9.66	$GdFe(CO_3)_2O$
	4	533.3–724.0	653.0	8.38	8.85	$GdFe(CO_3)_{2.5}O_{0.5}$
	5	724.0–984.1		1.47	1.47	$GdFe(CO_3)_{0.25}O_{0.75}$
	6	984.1–1018.0	974.7, 999.0	1.22	1.47	$GdFeO_3$

\*tart = dianion of tartaric acid; \*\*ox = dianion of oxalic acid

The infrared spectra of the decomposition oxides (except Eu–Fe compounds) consist in two absorption bands associated with stretching ( $\nu_s$ , in the range  $\sim 590\text{--}570\text{ cm}^{-1}$ ) and bending ( $\nu_b$ , in the range  $\sim 470\text{--}400\text{ cm}^{-1}$ ) vibrations of  $LnFeO_3$  [19] (Fig. 1b).

#### Characterization of the end products

The thermal decomposition of the investigated coordination compounds leads to end products which correspond to the molecular formula  $LnFeO_3$ , specific for ortho-ferrites. Well-crystallized pure mixed oxides (ex-

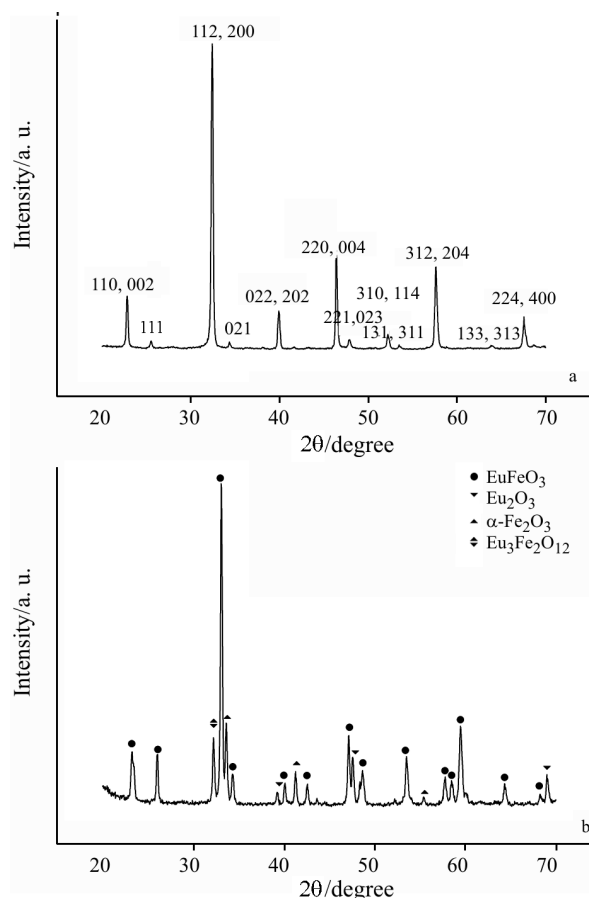


Fig. 3 XRD patterns of a – Ln–Fe and b – Eu–Fe oxides (thermal treatment 1 h at 1073 K)

cept Eu–Fe compound), as confirmed by X-ray diffraction analysis (Fig. 3a), were obtained after thermal treatment of 1 h at 1073 K. In the case of Eu–Fe compound, a mixture of complex oxides, namely ortho-ferrite ( $\text{EuFeO}_3$ ) and garnet ( $\text{Eu}_3\text{Fe}_2\text{O}_{12}$ ) together with  $\text{Eu}_2\text{O}_3$  and  $\alpha\text{-Fe}_2\text{O}_3$  (Fig. 3b) are detected).

## Conclusions

Ln–Fe ( $Ln=\text{La, Nd, Pr, Eu}$  and  $\text{Gd}$ ) polynuclear coordination compounds containing tartarate anion as ligand underwent a six steps thermal decomposition, via oxalate and oxocarbonate intermediates, leading to oxides corresponding to molecular formula  $\text{LnFeO}_3$ . An increase of the final decomposition temperature by  $\sim 120$  K ( $900.7 \rightarrow 1018.0$  K) as the ionic radius decreases from  $\text{La}^{3+}$  to  $\text{Gd}^{3+}$  ( $0.1061 \rightarrow 0.0938$  nm) is observed.

Pure  $\text{LnFeO}_3$  ( $Ln=\text{La, Nd, Pr}$  and  $\text{Gd}$ ) complex oxides were obtained after one hour of calcination at 1073 K. In similar condition, from Eu–Fe compound a mixture of mixed (ortho-ferrite ( $\text{EuFeO}_3$ ) and garnet ( $\text{Eu}_3\text{Fe}_2\text{O}_{12}$ )) and simple oxides ( $\text{Eu}_2\text{O}_3$  and  $\alpha\text{-Fe}_2\text{O}_3$ ) is obtained.

## References

- 1 S. Nakayama, *J. Mater. Sci.*, 36 (2001) 5643.
- 2 T. Premkumar and S. Govindarajan, *J. Therm. Anal. Cal.*, 84 (2006) 395.
- 3 W. Ferenc, A. Walków-Dziewulska and P. Sadowski, *J. Therm. Anal. Cal.*, 82 (2005) 365.
- 4 P. K. Gallagher, *Mater. Res. Bull.*, 3 (1968) 225.
- 5 S. Sadaoka, E. Traversa and M. Sakamoto, *J. Mater. Chem.*, 6 (1996) 1355.
- 6 E. Traversa, P. Nunziante, M. Sakamoto, Y. Sadoaka, M. C. Carotta and G. Martinelli, *J. Mater. Res.*, 13 (1998) 1335.
- 7 Y. Sadaoka, New development of Studies on Rare Earth Complexes (Report of a priority Area Program supported by the Ministry of Education, Science Sports and Culture, Japan), 1997, p. 785.
- 8 Y. Masuda, Y. Seto, X. Wang, Y. Yukawa and T. Arai, *J. Therm. Anal. Cal.*, 60 (2000) 1033.
- 9 Y. Sadaoka, E. Traversa and M. Sakamoto, *Chem. Lett.*, (1996) 177.
- 10 M. Sakamoto, Y. Komoto, H. Hojo and T. Ishimori, Nippon Kagaku Kaishi, (1990) 887.
- 11 O. Carp, L. Patron, A. Ianculescu, J. Pasuk and R. Olar, *J. Alloys Compd.*, 351 (2003) 314.
- 12 O. Carp, L. Patron, A. Ianculescu, D. Crisan, N. Dragan and R. Olar, *J. Therm. Anal. Cal.*, 72 (2003) 253.
- 13 L. Patron, O. Carp, I. Mindru and G. Grasa, *J. Therm. Anal. Cal.*, 56 (1999) 597.
- 14 V. Pocol, L. Patron, O. Carp, M. Brezeanu, E. Segal, N. Stanica and D. Crisan, *J. Therm. Anal. Cal.*, 55 (1999) 143.
- 15 K. Nakamoto, *Infrared and Raman Spectra of Inorganic Compounds*, Ed. 4, J. Wiley and Sons, 1986, p. 223.
- 16 R. M. Sharma and M. L. Kaul, *J. Indian Chem. Soc.*, 64 (1987) 459.
- 17 R. M. Sharma and M. L. Kaul, *J. Therm. Anal. Cal.*, 35 (1989) 2143.
- 18 C. D. Nenitescu, 'General Chemistry', Ed. Didactica, Bucharest, 1972, p.181.
- 19 J. T. Last, *Phys. Rev.*, 105 (1957) 1740.

DOI: 10.1007/s10973-006-8080-6