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Synthesis of citrates of selected lanthanides (Er, Ho and Lu)

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Abstract: Holmium, erbium and lutetium citrates can be synthesized by transforming freshly precipitated holmium, erbium and lutetium hydroxides in the citric acid solution under the hydrothermal conditions (above 100°C) after 3 days of reaction. In this paper in order to determine the synthesis conditions, the hydroxide and citrate stability areas of selected lanthanides were compared. The studies of the structure of the obtained holmium citrate, erbium and lutetium samples showed that these compounds crystallize in a monoclinic system. The crystallite sizes determined by the Halder-Wagner method were 67.8 ± 8.0 nm, 103.7 ± 4.5 nm and 68.1 ± 4.2 nm, respectively for the holmium citrate, erbium citrate and lutetium citrate samples. The shifts of the hydroxyl and carboxyl groups of citric acid in the FTIR spectrum indicate the interactions of both groups with holmium, erbium and lutetium cations. Then the obtained samples were subjected to the analysis of composition, and their particle size distribution was determined.

Keywords: PXRD diffraction, FTIR, citrates of (Er, Ho and Lu)

1. Introduction

New methods of synthesis and properties of lanthanide compounds with aliphatic hydroxy carboxylic acids are the subject of research in the context of their use as materials for superconductors, magnetic materials, catalysts and luminescent sensors, radiopharmaceuticals production (Baggio, et al., 2004, Zhou et al., 2008, Liu et al., 2005).

Yttrium and erbium citrate radiocolloids labeled with ^{90}Y and ^{169}Er , respectively, are recommended by the European Association of Nuclear Medicine for the treatment of rheumatoid arthritis using the radiosynovectomy method (EANM, 2003). This method generally uses beta-emitting radioisotopes. However, for the effective treatment of rheumatoid arthritis, new colloids and radioactive isotopes are being searched for (Schomäcker, 2015). Among other radioisotopes, single studies have been conducted in the treatment of rheumatoid arthritis using the ^{166}Ho isotope incorporated into the structure of boromacroaggregates (Kraft et al., 2005) or polymer microspheres (Mumper et al., 1992) and ^{177}Lu deposited in the hydroxyapatite structure (Banerjee et al., 2014). As in the case of radioisotopes ^{90}Y and ^{169}Er used in the form of yttrium citrate or erbium citrate radiocolloids in radiosynovectomy, it is possible to use radioisotopes ^{169}Ho and ^{177}Lu in the form of holmium citrate or lutetium radiocolloids, respectively. However, no methods of obtaining these citrates have been described in the literature so far.

Transition metal compounds with citric acid were used as precursors in the Pechini method for the preparation of barium titanate and cobalt (II) - iron (III) spinels, mixed zirconium oxide (Chandler et al., 1993, Gajbhiye et al., 1995, Petrova, 2006). Lanthanide citrates and actinides were also studied to improve lanthanide separation methods (Stewart 1955, Stevenson et al., 1961). Nevertheless, the synthesis of sparingly soluble lanthanide citrates, their structure and properties are not fully comprehensible. The attempts to determine the properties of these substances can be found in the papers by Babeshkin et al (Babeshkina et al., 1966a, Babeshkina et al., 1966b) but these are not detailed

studies in which the structure of the compounds was determined, the only exception are the papers cited earlier (Baggio, et al., 2004, Zhou et al., 2008, Liu et al., 2005).

In order to obtain uniform (monodisperse) colloid particles in the process of compound preparation the nucleation and subsequent processes of growth, dissolution, recrystallization and aggregation of crystals must be controlled. This can be achieved by controlling temperature in the reaction mixture, synthesis time and concentration of one of the synthesis reagents of the methods used to obtain monodisperse colloids for the synthesis of erbium and lanthanum citrates, transformation of the oxide in citric acid solution was applied.

This paper describes the synthesis of holmium citrate, erbium and lutetium based on the transformation of freshly precipitated holmium, erbium and lanthanum hydroxides, respectively. Then the obtained samples were subjected to analysis of composition, crystal structure by the PXRD method, FTIR tests and their granular distribution was determined.

2. Materials and methods

2.1. Synthesis of citrates of selected lanthanides and analysis of their composition and structure

2.1.1. Lanthanide citrate synthesis (Er, Ho or Lu)

The first stage of the method of obtaining lanthanide citrate (Er, Ho or Lu) is to prepare it as an intermediate lanthanide hydroxide (Er, Ho or Lu) according to the procedure given by Brzyska (1987).

2.1.2. Preparation of lanthanide hydroxides

60 ml of a 0.1M solution of lanthanide chloride (Er, Ho or Lu) provided by the Aldrich firm was placed in a beaker, adding the 0.1M NaOH solution in small portions until a pH of about 10 (pH = 10.07) was reached to obtain a precipitate. The resulting precipitate was then washed with redistilled water using the filter to obtain constant filtration conductivity.

2.1.3. Synthesis procedure of lanthanide citrates

0.1 M citric acid from the (Aldrich firm) solution was prepared. The washed lanthanide hydroxide was dispersed in a beaker in which 20ml 0.1 M citric acid was placed. The mixture was then sonicated for 3 minutes, the pH was measured and the suspension was placed in a Teflon autoclave for a period of 14 days at the 80, 100, 120 or 140° C. The obtained sample of lanthanide citrate was subjected to composition and structure analyses.

All chemical reagents used for the synthesis were 99.999% pure.

2.2. Experimental methods

The elemental analysis of erbium, holmium and lutetium citrate samples for the C and H contents was conducted using a Perkin-Elmer CHN analyzer. Besides the quantitative analysis of C and H contents, spectrometric studies of the obtained samples of lanthanide citrates were carried out using the FTIR Nicolet 8700A Thermo Scientific apparatus. The structure of the obtained preparations was examined by the XRD powder diffraction method using a Panalytical Empyrean apparatus. The particle size distribution of the obtained preparations was determined by the method of static light scattering using Malvern's Mastersizer 2000.

3. Results and discussion

In order to determine the synthesis conditions, the hydroxide and citrate stability areas of selected lanthanides were compared in this paper. These areas were obtained from the diagrams of hydroxides solubility based on the constant equilibrium of reactions given in Table 1 and the diagrams of lanthanide citrates solubility on the basis of the constant equilibria of the complexing reactions listed in Table 1 and the constant reactions listed in Table 2.

The comparison of the solubility of the amorphous hydroxides of selected lanthanides as well as erbium and holmium citrates as a function of pH is presented in Fig. 1. Since the data on the solubility product of lutetium citrate are not available in the literature, no solubility diagram has been constructed.

Table 1. Dissociation constants of hydroxocomplexes of selected lanthanides and solubility products of selected lanthanides hydroxides

	pK			Ref.
	Er	Ho	Lu	
$\text{Ln}(\text{OH})_{3(\text{am})} \leftrightarrow \text{Ln}^{3+} + 3\text{OH}^-$	23.0	24.2	23	Spahiu and Bruno,1995
$\text{LnOH}^{2+} \leftrightarrow \text{Ln}^{3+} + \text{OH}^-$	6.13	6.1	6.4	Spahiu and Bruno,1995
$\text{Ln}(\text{OH})_2^+ \leftrightarrow \text{Ln}^{3+} + 2\text{OH}^-$	12.1	11.9	12.3	Spahiu and Bruno,1995
$\text{Ln}(\text{OH})_3 \leftrightarrow \text{Ln}^{3+} + 3\text{OH}^-$	17.8	17.5	18.1	Spahiu and Bruno,1995
$\text{Ln}(\text{OH})_4 \leftrightarrow \text{Ln}^{3+} + 4\text{OH}^-$	23.4	22.47	24.05	Haas, et al., 1995

Table 2. Dissociation constants of citrate complexes of selected lanthanides and solubility products of citrates of selected lanthanides and dissociation constants of citric acid

	pK				Ref.
	H ⁺	Er	Ho	Lu	
$\text{LnCit}_{(\text{s})} \leftrightarrow \text{Ln}^{3+} + \text{Cit}^{3-}$	-	9.41	11.52	-	Gmelin, 1984
$\text{LnCit} \leftrightarrow \text{Ln}^{3+} + \text{Cit}^{3-}$	-	6.48	6.23	7.52	Gmelin, 1984
$\text{Ln}(\text{Cit})_2^{3-} \leftrightarrow \text{Ln}^{3+} + 2\text{Cit}^{3-}$	-	11.65	11.52	13	Gmelin, 1984
$\text{H}_3\text{Cit} \leftrightarrow \text{H}_2\text{Cit}^- + \text{H}^+$	3.13	-	-	-	CRC, 2003
$\text{H}_2\text{Cit}^- \leftrightarrow \text{HCit}^{2-} + \text{H}^+$	4.76	-	-	-	CRC, 2003
$\text{HCit}^{2-} \leftrightarrow \text{Cit}^{3-} + \text{H}^+$	6.4	-	-	-	CRC, 2003

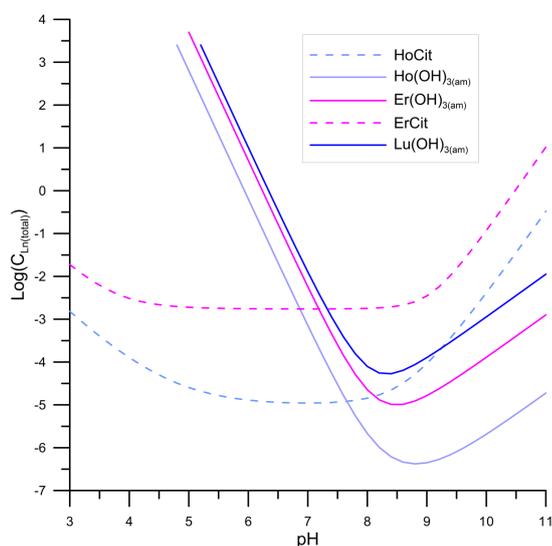


Fig. 1. Solubility of hydroxides of selected lanthanides as well as erbium and holmium citrates as a function of pH

As can be seen in Fig. 1, in the presented pH range amorphous erbium hydroxide is more difficult to dissolve above pH = 7.2 and the minimum solubility occurs at pH = 8.4. Erbium citrate is more difficult to dissolve to amorphous erbium hydroxide below pH 7.2, but its solubility over a wide pH range of 5 to 8.2 varies no more than 10% relative to the minimum solubility at pH 7. In this pH range, solubility is related to the dominance of the ErCit complex. In the case of the amorphous holmium hydroxide - holmium citrate system, the same solubility of both compounds is observed at pH = 7.67. Therefore, below this value, holmium citrate is more difficult to dissolve, and above that of amorphous holmium hydroxide the citrate is more difficult to dissolve. The minimum solubility of yttrium citrate

occurs at pH = 7, its solubility at this pH value is much lower than that of erbium citrate and around the minimum solubility changes not more than 10% in the pH range from 6.2 to 7.6. As can be seen from Fig. 1, amorphous lutetium hydroxide is more soluble than amorphous erbium hydroxide and its minimum solubility is found at pH = 8.4. Below this value, the hydroxide solubility increases rapidly. Although it is not possible to construct a solubility diagram for lutetium citrate, it can be assumed that, as in the case of erbium citrate and holmium citrate in an acidic environment, the lutetium citrate will be less soluble than lutetium hydroxide.

3.1. CH analysis of samples

The results of the holmium, erbium and lutetium citrate samples analysis from the hydrothermal transformation of freshly lost holmium, erbium or lutetium hydroxide in a citric acid solution are presented in Tables 3-5 in column 3 and 4, respectively.

The tables contain the results for the samples that had a crystal structure. The one before to last and last columns of Tables 3-5 show the calculated C and H contents for citrate monohydrate and dihydrate. As can be seen in the case of holmium citrate, (Table 3, column 3) the carbon content of the obtained samples is slightly larger than the calculation results, whereas the H content (column 4) corresponds to that calculated in that holmium citrate dehydrate sample. The larger carbon content in the obtained samples may be related to a content of adsorbed HoCit_2^{3-} complex which contains 26.4% C and 2.38% H in its composition. For erbium citrate samples, the carbon (column 3 in Table 4) and hydrogen (column 4 Table 4) contents are consistent with the those calculated for erbium citrate dihydrate. In the obtained samples of lutetium citrate at temperatures of 120, 130 and 140 °C, the content of carbon and hydrogen (column 3 and 4 respectively in Table 5) is close to that theoretically calculated for lutetium citrate dihydrate (Table 5).

Table 3. Results of C and H analyses for the HoCit samples obtained at 120 and 140°C

HoCit sample no	Synthesis temp. °C	Contents %		HoCit*H ₂ O		HoCit*2H ₂ O	
		% C	%H	% C	%H	% C	%H
1.	120	20.92	2.35				
2.	140	21.34	2.21	19.37	1.90	18.48	2.33

Table 4. Results of C and H analyses for the ErCit samples obtained at 140 and 160°C

ErCit sample no	Synthesis temp. °C	Contents %		ErCit*H ₂ O		ErCit*2H ₂ O	
		%C	%H	%C	%H	%C	%H
1	140	18.33	2.30				
2	160	18.94	2.29	19.25	1.88	18.37	2.31

Table 5. Results of C and H analyses for the LuCit samples obtained at 120, 130 and 140°C

LuCit sample no	Synthesis temp. °C	Contents %		LuCit*H ₂ O		LuCit*2H ₂ O	
		%C	%H	%C	%H	%C	%H
1	120	17.48	2.35				
2	130	17.81	2.09	18.87	1.85	18.02	2.27
3	140	18.00	2.11				

3.2 PXRD analysis

The investigations of the crystal structure of holmium citrate, erbium and lutetium samples using the PXRD method showed that the samples diffraction patterns are similar in terms of position and intensity of reflections (Fig. 2).

The obtained diffraction patterns were analyzed to determine the peaks location. Then using the Dicvol program (Boultif et al., 2004) cell parameters were determined and $M(2\theta)$ and $F(2\theta)$ (Wolff, 1968, Smith et al., 1979) values for the tested samples are presented in Table 6.

As follows from the analysis of the data in Table 6 very similar crystal structures were obtained in the citrates synthesis which is demonstrated by the similar volume of the unit cell and the similar values sometimes doubled of network constants. Moreover, the determined values of $M(2\theta)$ and $F(2\theta)$ parameters, with the exception of lutetium citrate, are high taking into account the fact that they are organometallic compounds.

Based on the diffraction patterns shown in Fig. 2, the average size of crystallites was determined on the basis of the peak location (θ) and width in the middle of the peak height (β) in the 2θ angle range

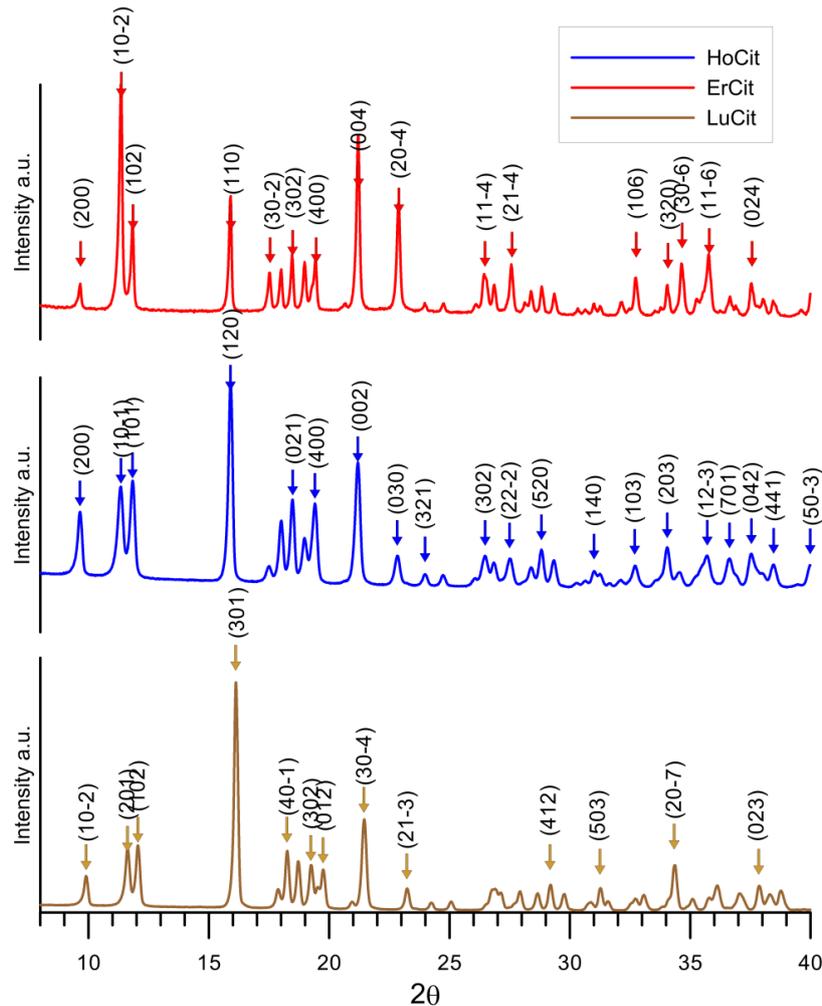


Fig. 2. XRD patterns of holmium, erbium and lutetium citrate samples

Table 6. Unit cell parameters of holmium, erbium and lutetium citrates

	HoCit	ErCit	LuCit.
a [nm]	1.8284(5)	1.8224(7)	1.9434(8)
b[nm]	1.1669(1)	0.5824(6)	0.5187(4)
c [nm]	0.8284(7)	1.6717(0)	1.8279(7)
β [°]	93.27	93.07	104.52
V [nm ³]	1.785(1)	1.772(1)	1.784(3)
$M(2\theta)$	23.8	19.1	6.9
$F(2\theta)$	51.2	43.9	13.9

Table 7. Crystallite sizes of holmium, erbium and lutetium citrate samples

Sample	Synthesis temp. °C	Mean crystal size [nm]	
		Halder-Wagner method	Scherrer method
HoCit	120	67.8 ± 8.0	60.3 ± 1.6
ErCit	140	103.7 ± 4.5	109.6 ± 8.4
LuCit	130	68.1 ± 4.2	71.8 ± 1.5

from 9° to 23° by the Halder-Wagner method (Halder et al., 1966, Oleszak et al., 2004) and the Scherrer (Leitao et al., 2016) methods for the peak at 16°. The obtained results of the crystallite size are collected in Table 7. As can be seen from the data in Table 7, the size of the crystallites of the tested samples within the error limits is the same for both methods. For the holmium citrate and lutetium samples, the average crystallite size is similar, while for ErCit synthesized at 140°C the average crystallite size exceeds 100nm.

3.3. FTIR analysis

The FTIR spectra of the obtained samples of holmium citrate, erbium and lutetium are presented in Fig. 3 and for comparison, the FTIR citric acid spectrum is also given. The gift spectra in the 2500-3700cm⁻¹ wave number range show a wide band associated with vibrations of water molecules, water hydroxyl group at 3450cm⁻¹ and citric acid hydroxyl group at 3492cm⁻¹. As one can see, the spectra of holmium, erbium and lutetium citrates are similar but in compared to citric acid, there is a shift in the characteristic asymmetrical vibration bands of the C = O citric group at the wavenumbers 1175 and 1698 cm⁻¹ towards the lower values, i.e. 1658 and 1605 cm⁻¹. This effect is better visible in Fig. 4. A similar shift effect was observed for the other metal citrates (Miller et al., 2015, Jumanath et al., 2019, Gajbhiye et al., 1996, Gajbhiye et al., 1995). The difference between the asymmetrical (1658 and 1605 cm⁻¹) and symmetrical (1420 cm⁻¹ and 1397cm⁻¹) vibrations indicates that one citrate ion coordinates one metal atom (Raju et al., 2017).

However, Zhou et al. showed (Zhou et al. 2008) that erbium ions are combined with four citrate ion ligands forming a two-dimensional network of erbium citrate monohydrate. The 2D layers interact with the hydrogen bonding to create a 3D supramolecular network. The interactions between the functional groups (carboxyl and hydroxyl groups) of citrate ligands and the erbium cation result in its 8 coordination site, and the 9 coordination site is occupied by a water molecule. As a result of these interactions in the IR spectrum, there can be shifts in characteristic bands not only of carboxyl but also hydroxyl groups. The analysis of the remaining bands of the FTIR spectrum presented in Fig. 3 confirmed the shifts or disappearance of bands characteristic of citric acid. The list of characteristic bands for holmium, erbium and lanthanum citrates and for citric acid sesquihydrate is given in Table 8.

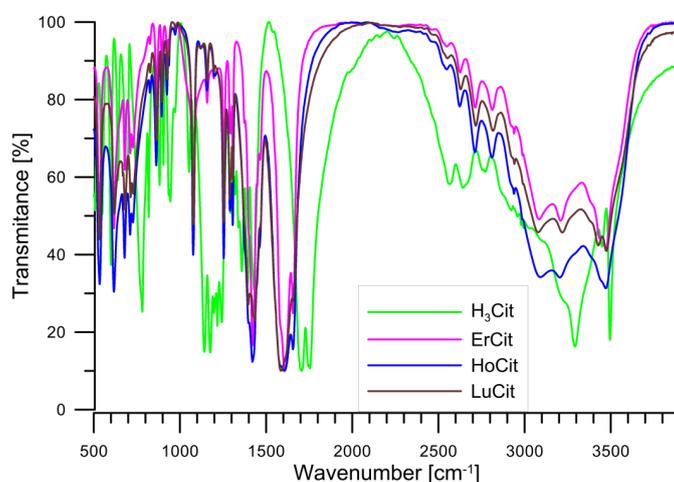


Fig. 3. FTIR spectrum of holmium, erbium and lutetium citrate samples

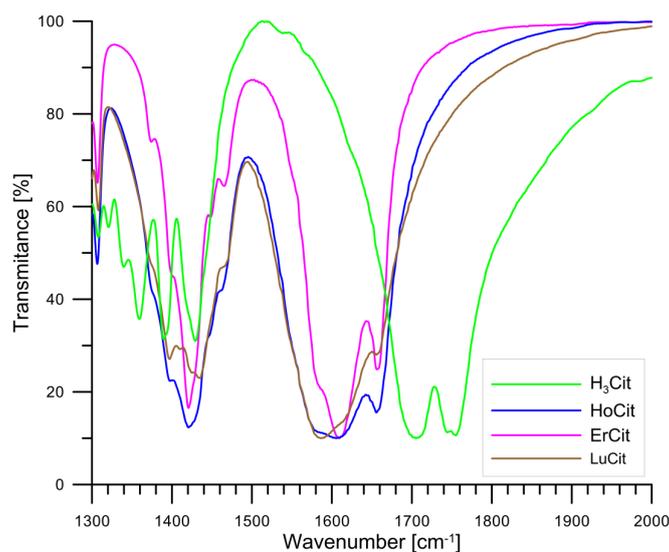


Fig. 4. FTIR spectrum of holmium, erbium and lutetium citrate samples in the range 1300-2000 cm^{-1}

As it results from the positions of the bands listed in Table 8, apart from changing the position of the bands characteristic of carboxyl groups vibrations, there is a shift in the position of the hydroxyl group of citric acid from 3498cm^{-1} to 3474cm^{-1} . The shifts of wavenumbers characteristic of hydroxyl and carboxyl groups indicate their interaction with holmium, erbium or lutetium cations.

3.4. Particle size distribution of LnCit

Fig. 5 presents the numerical distribution of the particles of the obtained holmium, erbium and lutetium citrates. As can be seen, the grain distribution of erbium and holmium citrates coincides practically. The grain distribution of lutetium citrate is slightly shifted towards larger grain sizes and a small peak appear as a result of sizes the grain fraction with a maximum at $30\ \mu\text{m}$. The table contains the values of diameters characterizing the discussed distributions. The data in Table 9 confirm the similarity of the grain distribution of holmium and erbium citrates samples as well as the larger particle sizes of lutetium citrate compared to HoCit and ErCit. The comparison of the particle sizes of holmium, erbium and lutetium citrates, (Table 9) with the crystal sizes (Table 7) indicates that the particles are crystal aggregates.

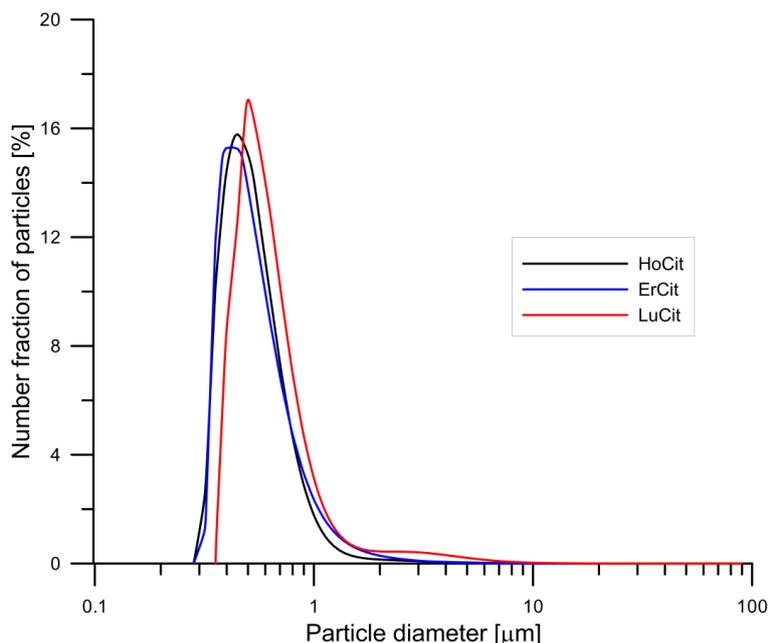


Fig. 5. The number of particle sizes distribution of holmium erbium and lutetium citrates samples

Table 8. Observed wavenumbers (cm⁻¹) and assignments for holmium, erbium and lutetium citrates and citric acid sesquihydrate

HoCit	ErCit	LuCit	H ₃ Cit1.5*H ₂ O	Assignment	Ref.
3470.28	3471.72	3474.62	3495.83	v (O-H) hydroxyl	(Gajbhiye et al., 1995)
3451.47	3438.46	3427.37	3450.03	v O-H (water)	(Gajbhiye et al., 1995)
2938.02	2938.98	2940.43		v _{asym} (CH ₂)	(Bichara et al.,2012)
			1754.90	v _{asym} (C=O)	(Bichara et al.,2011)
			1705.25	v _{asym} (C=O)	(Bichara et al.,2011)
1655.59	1656.55	1644.02		v _{asym} (COO ⁻)	(Bertoli et al., 2015)
1605.45	1609.31	1586.16		v _{asym} (COO ⁻)	(Bertoli et al., 2015)
1420.80	1420.80	1435.26	1428.99	v _{sym} (COO ⁻)	(Bertoli et al., 2015)
			1389.46	v _{sym} (COO ⁻) + δ _{sciss} (HOH)	(Bertoli et al., 2015)
			1359.09	v _{sym} (COO)	(Bertoli et al., 2015)
			1339.80	δ _{wagging} (HCH)	(Bertoli et al., 2015)
1306.54	1307.02	1307.98	1320.52	τ (CH ₂)	(Bertoli et al., 2015)
			1307.98	δ _s (COH)	(Bertoli et al., 2015)
1290.14	1295.93	1288.70	1292.56	δ _{wagging} (HCH)	(Bertoli et al., 2015)
1254.47	1254.95	1254.95	1242.90	δ _{rocking} ((HCH)+ v (CC)+ v (CO)	(Bertoli et al., 2015)
1230.36	1197.10	1230.36	1217.34	δ _{sciss} (HCH)	(Bertoli et al., 2015)
			1198.06	v (C-O)	(Bertoli et al., 2015)
1157.08	1158.04	1159.49	1175.88	v (CO)	(Bichara et al.,2012 (Bertoli et al., 2015)
			1141.65	v (CO)	
1077.05	1077.53	1079.46	1081.87	δ _{rocking} ((HCH)+ v(CC)	(Bertoli et al., 2015)
			1052.94	v (C-O)	
971.95	972.91	974.84	970.98	v C-C	(Bertoli et al., 2015)
			943.98	v (C-O)	(Bertoli et al., 2015)
936.27	936.75	937.23			
925.18	925.66	926.15			
893.84	894.33	895.29	904.45	v (C-C)	(Bertoli et al., 2015)
			882.27		
862.99	864.44	865.88			
826.35	825.87	827.31		v (C-C)	(Bertoli et al., 2015)
			781.99	v (C-C)	(Bertoli et al., 2015)
727.03	728.00	728.96			
711.12	711.60	714.01			
678.82	680.27	682.20			
			641.21	τ (OH)	(Bertoli et al., 2015)
617.11	617.11	620.48			
			598.79	τ (OH)	(Bertoli et al., 2015)
534.19	533.70	533.22	549.61	τ (OH)	(Bertoli et al., 2015)
			507.19		

δ_{twist} - twisting deformation, δ_{rocking} - rocking deformation, δ_{wagging} - wagging deformation; δ_{sciss} - scissors deformation; v_{sym} - symmetric stretching, v_{asym} - asymmetric stretching, v - stretching, τ - torsion

Table 9. Characteristics of the particle size diameters distribution

	HoCit	ErCit	LuCit
d(0.1) [μm]	0.35	0.35	0.41
d(0.5) [μm]	0.47	0.47	0.55
d(0.9) [μm]	0.75	0.84	0.96
$d_{\max} \pm \sigma$ [μm]	0.57 ± 0.37	0.59 ± 0.35	0.75 ± 0.75

d(0.1) diameter below which 10% of the fraction falls,

d(0.5) diameter below which 50% of the fraction falls,

d(0.9) diameter below which 90% of the fraction falls,

d_{\max} - diameter corresponding to the peak maximum,

σ - standard deviation of the distribution.

4. Conclusions

Holmium, erbium and lutetium citrates in the crystalline form can be obtained by transforming freshly precipitated holmium, erbium and lutetium hydroxides in the citric acid solution under the hydrothermal conditions (above 100°C) after 3 days of reaction. The elemental analysis for the carbon and hydrogen contents showed that, the samples of holmium citrate dihydrate, erbium citrate and lutetium citrate were obtained as a result of the synthesis. The shifts of the hydroxyl and carboxyl groups of citric acid in the FTIR spectrum indicate the interactions of both groups with holmium, erbium and lutetium cations. The studies of the structure of the obtained samples of holmium, erbium and lutetium citrates showed that these compounds crystallize in a monoclinic system. The crystallite size determined by for the holmium citrate, erbium citrate and lutetium citrate samples Halder-Wagner method were $67.8 \pm 8.0\text{nm}$, $103.7 \pm 4.5\text{nm}$ and $68.1 \pm 4.2\text{nm}$, respectively.

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