Journal of Thermal Analysis, Vol. 45 (1995) 199-206

PREPARATION AND THERMAL BEHAVIOUR OF RARE EARTH CITRATE HYDRATES

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Abstract

Nine rare earth citrate hydrates ($RE(C_6H_5O_7)\cdot nH_2O$, RE=La, Nd, Sm) were prepared and characterized by chemical analysis, elementary analysis, thermal analysis and IR spectra. The thermal decomposition processes were studied by using TG-DTG and IR spectra techniques. Dehydration enthalpies and dehydration entropies of 3 neodymium and 3 samarium citrate hydrates were also determined by means of DSC.

Keywords: dehydration enthalpy, dehydration entropy, rare earth citrate, thermal decomposition

Introduction

The thermal decomposition of citrates, tartrates, lactates and oxalates of metals has usually been used as a method of preparing the ultrafine powders of functional ceramics. The special performances of the powders in magnetic activity, thermal resistance, light absorption, chemical activity, catalytic activity and low-melting, make their vast applications in research fields and in the development of new fine ceramic materials possible. Thus, the preparation of ultrafine ceramic powders by thermal decomposition of organic salts of metals has been used widely [1–5].

The rare earth citrates have been used in preparing the original powder material ($REGaO_3$) for preparing the high temperature superconducting substrate in our laboratory. Papers [6–7] on the preparation of the citrates were published, but their thermal behaviours have not been known in detail, especially the thermodynamic data on the dehydration of the citrate hydrates still have not been revealed. In this paper, nine rare earth citrate hydrates were prepared and studies were made on their thermal decomposition and thermodynamics of their

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0368–4466/95/ $ 4.00

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studies were made on their thermal decomposition and thermodynamics of their dehydrations. This is of great significance in promoting the preparation of ultrafine ceramic powder.

Experimental

Reagents

La_2O_3 (99.9%), Nd_2O_3 (99.99%), Sm_2O_3 (99.5%) were all from Shanghai Yuelong Chemical Factory, nitric acid and ammonium citrate are of A. R. grade.

Preparations

The method of preparing lanthanum, neodymium and samarium nitrate hexahydrates was as described in ref. [8].

The preparations of these solid citrates were as follows: equal volumes of 0.1 mol/dm^3 rare earth nitrate and 0.1 mol/dm^3 ammonium citrate were mixed, and the flocculent precipitates of rare earth citrates were obtained. The precipitations were kept in a hot water bath for 6–8 h, aged at room temperature for 5–6 days and nights, then filtered off through the sintered glass crucible, and washed with twice-distilled water until no nitrate was detected in wash water by diphenylamine sulfonate. After the precipitates were washed with alcohol, dried in drying box to expel all alcohol, ground, screened to 200 mesh. The obtained rare earth citrates were again dried to constant weight under different drying conditions at room temperature.

Analysis and apparatus

Dehydration enthalpies and dehydration entropies were recorded using DSC DuPont 9900 thermal analyser, with a heating rate of 10 deg·min^{-1} in a flow of nitrogen. Water contents and thermal decomposition processes were determined using TG-DTG DuPont 9900, with a heating rate of 10 deg·min^{-1} in static air. Rare earth elements were estimated gravimetrically as oxides. C, H, N contents were determined using P-E 2400 elementary analyser. The drying condition, colour and composition of the citrate hydrates were all listed in Table 1.

Results and discussion

Thermal decomposition processes of rare earth citrate hydrates

The nine rare earth citrate hydrates decomposed in five similar steps (for La and Nd) or in four similar steps (for Sm). Here, the thermal decomposition

Table 1 Drying condition, colour and composition of the rare earth citrate hydrates

Hydrate	Drying condition	Colour	RE /%		C /%		H /%		xH_2O	
			Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
$LaCit \cdot 1.75H_2O$	P_2O_5	white	38.78	38.64	19.46	20.05	2.44	2.36	1.69	1.75
$LaCit \cdot 2.25H_2O$	35% H_2SO_4	white	37.89	37.69	19.23	19.55	2.50	2.57	2.16	2.25
$LaCit \cdot 4.25H_2O$	Sat. NH_4Cl	white	34.43	34.34	17.77	17.82	2.95	3.34	4.12	4.25
$NdCit \cdot 2.5H_2O$	98% H_2SO_4	faint vio.	38.49	38.12	18.62	19.05	2.68	2.64	2.64	2.5
$NdCit \cdot 3H_2O$	50% H_2SO_4	faint vio.	37.17	37.23	18.12	18.61	2.74	2.84	3.01	3
$NdCit \cdot 3.25H_2O$	35% H_2SO_4	faint vio.	36.79	36.80	17.81	18.39	2.77	2.94	3.18	3.25
$SmCit \cdot 1.5H_2O$	98% H_2SO_4	faint yel.	41.58	41.04	18.92	19.66	2.39	2.18	1.65	1.5
$SmCit \cdot 3H_2O$	50% H_2SO_4	faint yel.	38.02	38.22	17.67	18.31	2.73	2.80	3	3
$SmCit \cdot 4H_2O$	35% H_2SO_4	faint yel.	36.66	36.55	16.89	17.49	3.19	3.16	3.89	4

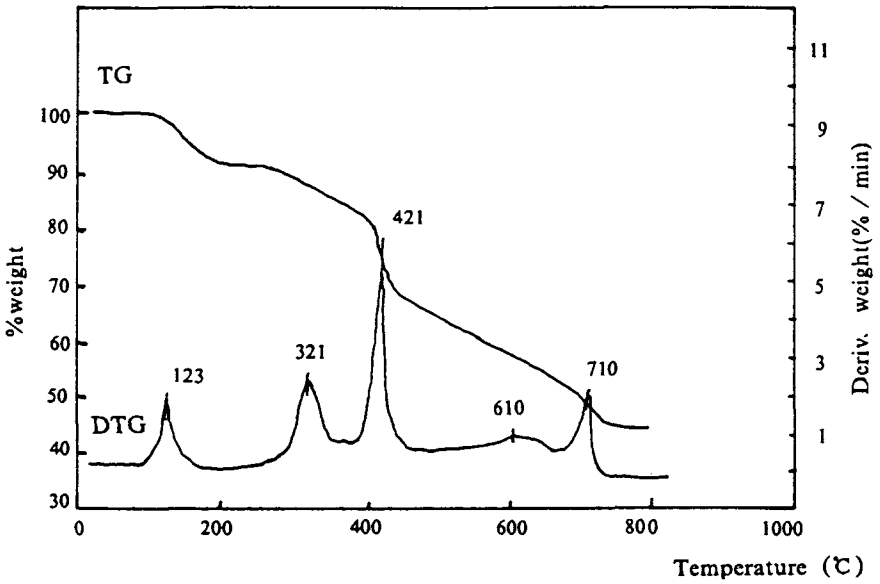

Fig. 1 TG-DTG curve of $LaCit.1.75H_2O$

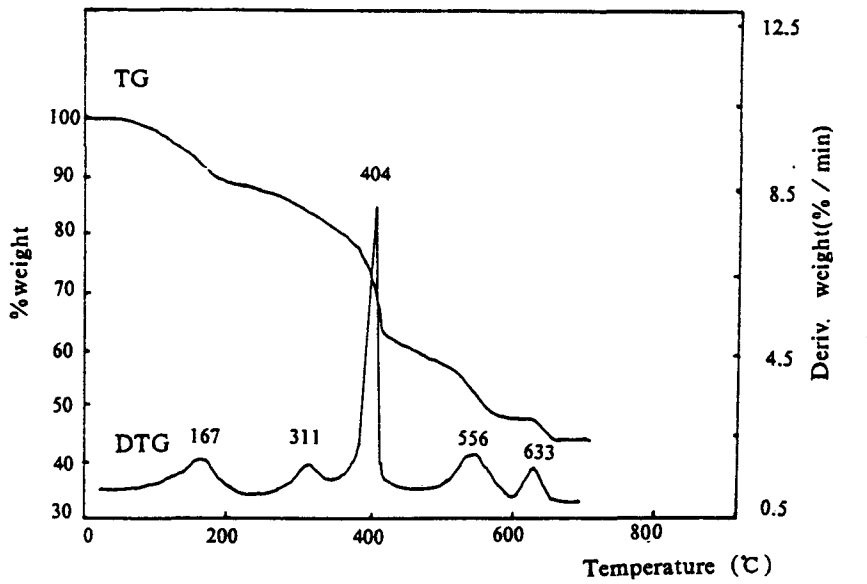

Fig. 2 TG-DTG curve of $NdCit.2.5H_2O$

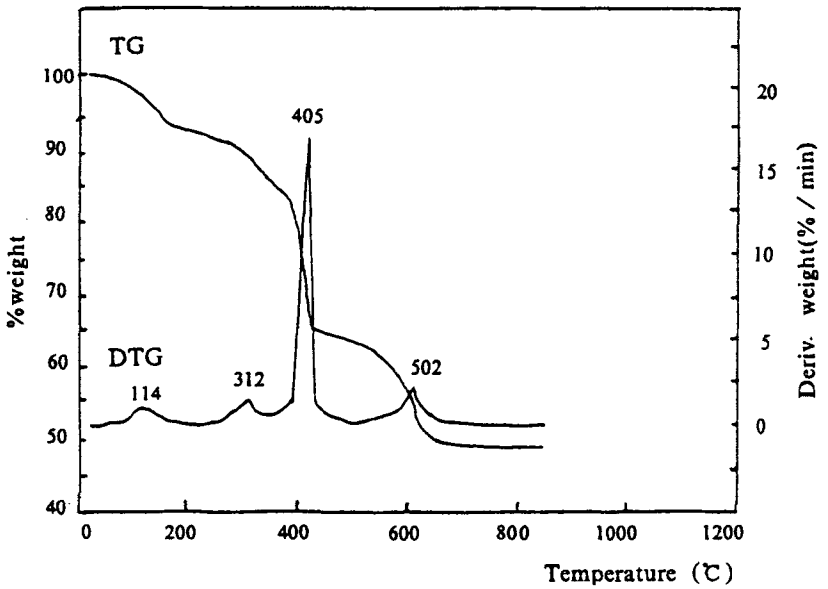

Fig. 3 TG-DTG curve of $SmCit.1.5H_2O$

curves for $La(C_6H_5O_7)\cdot 1.75H_2O$, $Nd(C_6H_5O_7)\cdot 2.5H_2O$, $Sm(C_6H_5O_7)\cdot 1.5H_2O$ as typical examples were shown in Figs 1, 2 and 3.

According to the data from the TG-DTG curves in Figs 1–3, the first two decomposition stages of each hydrate were affirmed to be the dehydration (including the lattice water of $C_7H_5O_7^{3-}$) which all ended at about 350°C.

The intermediate products of the third stage for the three hydrates were taken out and analysed by IR technique. Their absorptions at 1490 cm^{-1}(s), 1050 cm^{-1} and 820 cm^{-1} correspond to the vibration of carbonate (CO_3^{2-}), indicating that the intermediate products were carbonates. The weight losses in this stage were: Obs. 21.76%, Cal. 22.55% for La; Obs. 19.41%, Cal. 21.42% for Nd; Obs. 22.32%, Cal. 22.13% for Sm, again confirming the formation of the rare earth carbonates.

The decomposition products in the fourth stage for the La and Nd, were considered to be different from that of the fourth stage for Sm, the formers were $La_2O_2CO_3$ and $Nd_2O_2CO_3$, but the latter was Sm_2O_3. This assumption was confirmed from the following experimental data. A weight loss of 11.10% in the fourth stage was comparable to the calculated value of 12.24% for La, the product absorption peaks at 1510 cm^{-1}, 1445 cm^{-1}, 1335 cm^{-1} and at 870 cm^{-1}, 840 cm^{-1} were respectively characteristics of the band (γ_{CO}) and the band (δ_{CO_3}) [9]. A weight loss of 11.39% in the fourth stage was in good agreement with

Table 2 Dehydration enthalpies and dehydration entropies of Neodymium citrate hydrates and Samarium citrate hydrates

Hydrate	Loss of hydrate water /mol	DSC /K		Dehydration enthalpy	Dehydration entropy
		T_e	T_p	$kJ\cdot(mol\cdot H_2O)^{-1}$	$J\cdot(mol\cdot H_2O\cdot K)^{-1}$
$NdCit\cdot 2.5H_2O$	2.5	458.4	486.0	23.59	48.53
$NdCit\cdot 3H_2O$	3	467.9	492.2	18.69	37.98
$NdCit\cdot 3.25H_2O$	3.25	465.2	491.3	20.14	40.99
$SmCit\cdot 1.5H_2O$	1.5	380.4	435.3	25.02	57.47
$SmCit\cdot 3H_2O$	3	363.4	411.9	36.64	88.97
$SmCit\cdot 4H_2O$	4	349.2	400.7	45.71	114.10

the calculated value of 11.63% for Nd, the product absorption peaks at 1520 cm^{-1}, 1460 cm^{-1}, 1360 cm^{-1} and at 870 cm^{-1}, 840 cm^{-1} were characteristics of the band (γ_{CO}) and the band (δ_{CO_3}), respectively. The characteristic IR absorption spectra of the fourth stage product for Sm were in good agreement with the standard IR spectra of Sm_2O_3 [10].

The characteristic IR spectra of the fifth stage products for La and Nd also agree well with the reported IR spectra of La_2O_3 [10] and Nd_2O_3 [11].

In accordance with the IR spectra and TG-DTG experiments described

$$LaCit\cdot 1.75H_2O \xrightarrow{48-180} LaCit\cdot H_2O \xrightarrow{224-371} La(C_6H_3O_6) \xrightarrow{371-519}$$

$$La_2(CO_3)_3 \xrightarrow{519-657} La_2O_2CO_3 \xrightarrow{657-736} La_2O_3$$

$$NdCit\cdot 2.5H_2O \xrightarrow{19-233} NdCit \xrightarrow{233-348} Nd(C_6H_3O_6) \xrightarrow{348-457}$$

$$Nd_2(CO_3)_3 \xrightarrow{457-571} Nd_2O_2CO_3 \xrightarrow{571-690} Nd_2O_3$$

$$SmCit\cdot 1.5H_2O \xrightarrow{31-214} SmCit \xrightarrow{214-344} Sm(C_6H_3O_6) \xrightarrow{344-467}$$

$$Sm_2(CO_3)_3 \xrightarrow{467-737} Sm_2O_3$$

above, we can preliminarily assume that the thermal decomposition processes for these rare earth citrate hydrates are as follows.

The thermal decomposition pathway of the hydrate for Sm display only four steps, the reason might be that the radius of Sm^{3+} ion is smaller than those of La^{3+} and Nd^{3+} ions, so that the polarizing powder of Sm^{3+} ion might be stronger for the adjacent oxygen atom in the carbonate ion, the binding force between the oxygen atom and the carbon atom in the carbonate ion would thus be too much weakened to form the intermediate, $Sm_2O_2CO_3$.

Dehydration enthalpies and entropies of rare earth citrate hydrates

According to the data from TG and DSC curves of the nine hydrates, the dehydration of the three kinds of hydrates of lanthanum citrate involves two steps: first, the loss of part of water of crystallization, and then the loss of the remaining water of crystallization and lattice water. Water in the other two citrates were lost in one step. Therefore only the dehydration entropies and dehydration enthalpies of six of the nine citrates were determined. The results were listed in Table 2.

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The authors gratefully acknowledge the financial Support from the Shaanxi Province Natural Science Foundation.

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Zusammenfassung — Es wurden neun Seltenerdenzitrathydrate ($RE(C_6H_5O_7)nH_2O$, RE=La, Nd, Sm) hergestellt und mittels chemischer Analyse, Elementaranalyse und IR-Spektren charakterisiert. Der Prozeß der thermischen Zersetzung wurde mittels TG-DTG und IR-Spektren untersucht. Mittels DSC wurden außerdem die Dehydratationsenthalpien und Dehydratationsentropien von 3 Neodym- und von 3 Samariumzitrathydraten bestimmt.