ELSEVIER
Thermochimica Acta 258 (1995) 135–144
thermochimica
acta

The preparation of yttrium oxide from a $Y(N_2H_3COO)_3 \cdot 3H_2O$ precursor in various atmospheres

A. Rahten, J. Maček *, B. Novosel

University of Ljubljana, Jožef Stefan Institute and Department of Chemistry and Chemical Technology, 61000 Ljubljana, Slovenia

Received 20 September 1994; accepted 10 December 1994

Abstract

The thermal decomposition of yttrium hydrazidocarbonate trihydrate $Y(N_2H_3COO)_3 \cdot 3H_2O$ has been studied in the temperature range 25–1400°C. The influence of inert and oxidative atmospheres, e.g. argon, carbon dioxide and air, on the course of the thermal decomposition was determined. After dehydration to the anhydrous compound, the decomposition proceeds through several decomposition steps to yttrium oxide. In air, a pure high temperature C form of this oxide is isolated at a relatively low temperature, e.g. 708°C. The same end product is obtained in carbon dioxide, albeit at higher temperatures, but in argon the yttrium oxide is mixed with amorphous carbon. The surface area and other particulate properties are substantially dependent on the heating programme of the sample.

Keywords: DTA; EGA; TG; Yttrium hydrazidocarbonate trihydrate; Yttrium oxide

1. Introduction

The use of hydrazidocarbonates as precursors for the preparation of metal powders or oxide materials has been suggested in some earlier papers [1]. The composition of the intermediates and end products is extensively determined by the chemical composition of these precursors, the nature of the cation and the atmosphere used in the thermal decomposition experiments. The inclusion of a strong reducing group in the molecule of the initial compound, namely hydrazidocarbonate, which is a derivative of the even more powerful reducing agent hydrazine, plays an important role in the course of

---

* Corresponding author.

SSDI 0040-6031(94)02245-3

decomposition reactions. In an inert atmosphere, strongly reducing conditions set in during the decomposition and, in the case of easily reducible cations, cause the formation of metal powder. However, the nature of the cation, e.g. a high redox potential, can prevent this, and in such cases the decomposition proceeds either to the oxide or to a more complex end product.

Oxidising atmospheres extensively influence the course of the decomposition reactions. They oxidise the hydrazido group to nitrogen and water (ammonia) and thus prevent the formation of the metal even in cases when it would be possible. Under such conditions the appropriate oxide is obtained.

Ultra-fine ferrites, cobaltites and oxides were prepared by the decomposition of solid solutions of $N_2H_5[M(N_2H_3COO)_3]\cdot 3H_2O$-type precursors (M being Mg, Mn, Fe, Co, Ni or Zn) [2].

Thermal decomposition of $N_2H_5[M(N_2H_3COO)_3]\cdot 3H_2O$ (M being Fe, Co or Ni) or $M(N_2H_3COO)_3\cdot xH_2O$ (M being Co or Cu, $x=0$ or 0.5) yielded reactive metal powders [3]. The advantage of the use of such precursors is the relatively low temperature for the isolation of oxides (200–300°C in air) and metal powders (300–450°C). The transformation reactions of the hydrazidocarbonate are accelerated by the catalytic, autocatalytic and/or oxidative decomposition of hydrazine. A large amount of gas is released and therefore an end product with very high porosity and surface area is obtained.

Particles of CeO_2 with specific surface area 90 $m^2\,g^{-1}$ were prepared by combustion synthesis [4].

The field of fine ceramic powders of rare earth elements is of particular interest. The thermal properties of $Y(N_2H_3COO)_3\cdot 3H_2O$ were therefore studied in different atmospheres in order to explain the decomposition reactions and possibly to isolate new intermediates and final product and to determine their characteristics.

2. Experimental

Yttrium hydrazidocarbonate trihydrate was prepared according to published information [5] by the addition of concentrated yttrium trichloride solution to a very diluted solution of hydrazine that was previously saturated with carbon dioxide.

The hydrazine content was determined by potentiometric titration with KIO_3 [6], and ammonia was determined by the Kjeldahl method. The yttrium content was determined by direct complexometric titration at pH 5.5–5.6 in the presence of Arsenazo III [7, 8] indicator. Volumetric titration was used for the determination of carbon dioxide [9]. The cyanide content was determined by distillation in an excess of mineral acid as tetracyanonickelate [10], and the content of cyanate ion as ammonium salt in alkaline media [11].

Mettler thermoanalyser TA-1 and Netzsch STA 409 instruments were used for analysis of the thermal properties of the precursor in atmospheres of dry argon (purified by Messer Griesheim Hydrosorb and Oxisorb cartridges), air and carbon dioxide. A temperature range of 25–1400°C and a heating rate of 4 K min^{-1} were used. Samples of mass 100 mg were used except in the case of evolved gas analysis (EGA) when an

Inficon Leybold Heraeus Quadrex 200 quadrupole mass spectrometer was connected to the Netzsch STA 409. In the latter case 1000 mg samples were employed.

X-ray powder diffraction data were obtained using a Guinier de Wolff type camera and Cu $K\alpha$ radiation. For the identification of the products, the CD-ROM database PDF2 set 1–39 was used. IR spectra were recorded on a Perkin-Elmer FTIR 1710 spectrometer. Specific surface area measurements were made according to the BET method with a Ströhlein area meter, and the particle size of the products was determined with a Fritsch Analysete 22 laser particle sizer.

3. Results and discussion

The chemical composition of the yttrium precursor $Y(N_2H_3COO)_3 \cdot 3H_2O$ was determined as: N_2H_4 26.2(±0.05)%, Y 23.9(±0.05)%, CO_2 36.0(±0.2)%, H_2O 14.7% (calculated by difference from 100%); required values: N_2H_4 26.12%, Y 24.15%, CO_2 35.87%, H_2O 14.68%).

Thermal decomposition was studied in an inert dry argon atmosphere and in air and carbon dioxide. The argon atmosphere was used to determine the decomposition without interaction with the furnace atmosphere, air to observe and study the course of the oxidation reactions, and carbon dioxide to determine the possible influence of this gas on the equilibrium decomposition reactions.

The nature of the yttrium hydrazidocarbonate trihydrate (the reactivity of its constituents, an extensive number of possible combinations and recombinations of the elements present) led to very complex decomposition sequences. From the TG curves alone the decomposition cannot be elucidated, therefore chemical analysis of the intermediates, evolved gas analysis and other methods were also employed.

Intermediates of the thermal decomposition in different atmospheres were prepared by maintaining the samples at a preselected temperature for 6 h. Longer time intervals were chosen in order to enhance the crystallinity of the intermediates and thereby facilitate their analysis by X-ray powder diffraction. The sample mass in this case was 1000 mg.

The decomposition of yttrium hydrazidocarbonate trihydrate in dry argon proceeds in four steps, as shown in Fig. 1 and Table 1.

The first step of the decomposition is the dehydration of the sample. The observed weight loss for this particular step is 17.8%, as compared with the calculated weight loss of 14.68%. This discrepancy between the obtained and the calculated value is observed also in the other two atmospheres, the weight loss in air being 3.72% higher than calculated and that in carbon dioxide higher by 2.12%.

This excess weight loss in the dehydration step was also observed in the dehydration of the similar neodymium and other lanthanide hydrazidocarbonate trihydrates [12]. The complete structural analysis of yttrium or other hydrazidocarbonate trihydrates could not be achieved, owing to difficulties in the preparation of single crystals, and thus the exact bonding or arrangement of water molecules in the compounds is unknown. The dehydration somehow disrupts the whole structure and is accompanied, to a lesser extent, by the decomposition or pyrohydrolysis of the hydrazidocarbonate

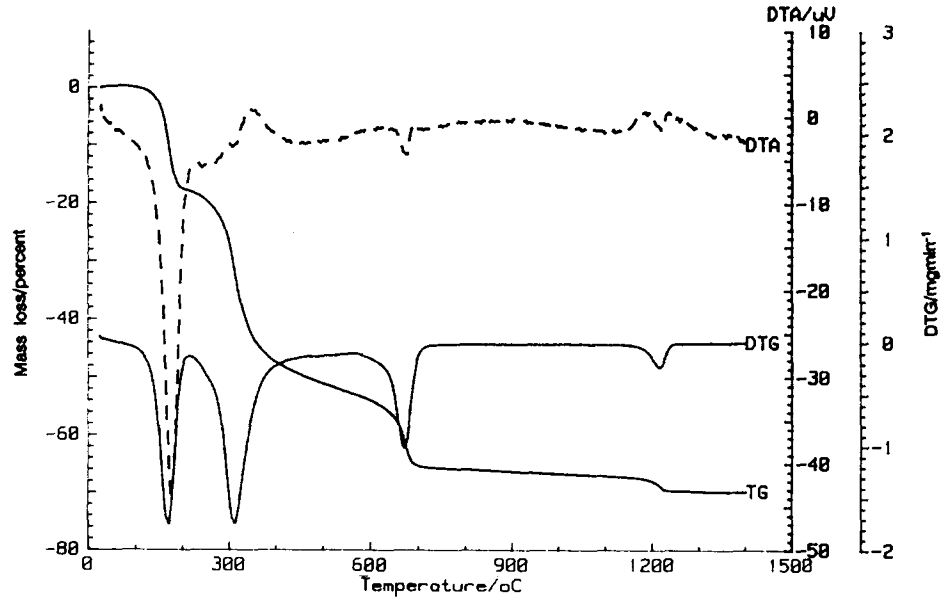

Fig. 1. TG/DTG/DTA curves of $Y(N_2H_3COO)_3 \cdot 3H_2O$ in Ar.

Table 1
Thermal decomposition of $Y(N_2H_3COO)_3 \cdot 3H_2O$ in Ar, air and CO_2

		Temp. int./°C	Wt. loss/%	DTA/°C	DTG/°C
Step I	Ar	25–203	17.8	175 (endo)	170
	Air	25–187	18.9	173 (endo)	169
	CO_2	25–200	16.8	177 (endo)	172
Step II	Ar	203–456	32.0	337 (exo)	310
	Air	187–280	32.5	247 (exo)	242
	CO_2	200–384	22.2	328 (exo)	315
Step III	Ar	456–713	15.9	671 (endo)	672
	Air	280–703	18.3	–	660
	CO_2	384–712	25.9	660 (endo)	664
Step IV	Ar	713–1400	4.2	1218 (2 exo)	1217
	CO_2	712–1300	6.1	1127 (endo)	1053

group. Water can either co-ordinate to the central cation, as is the case for manganese hydrazidocarbonate dihydrate [13], or can be hydrogen bonded to the co-ordination polyhedron around the metal cation. The partial decomposition of hydrazidocarbonato groups accompanying the dehydration was confirmed by EGA (Fig. 2). The evolution of water is accompanied by the evolution of small amounts of ammonia and a gas with a molecular mass of 28, e.g. nitrogen or carbon monoxide.

The dehydration step proceeds similarly in the other two atmospheres. The differences in weight loss are in all three cases minor, and therefore it is speculative to relate

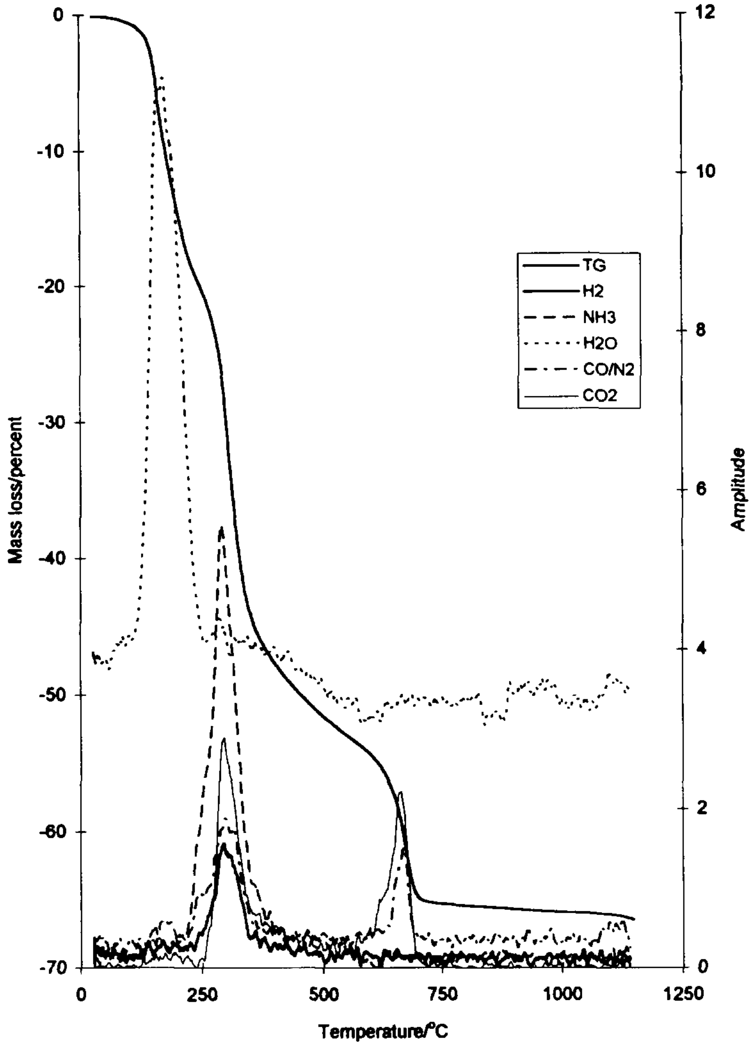

Fig. 2. EGA curves of $Y(N_2H_3COO)_3 \cdot 3H_2O$ in Ar.

them to the actual influence of the furnace atmosphere. However, it can be assumed that carbon dioxide stabilises the hydrazidocarbonate group and that the presence of oxygen destabilises it.

The results of the chemical analysis of the step I intermediates are given in Table 2. The IR spectra of thermally dehydrated samples are identical for the samples prepared in all three atmospheres. X-ray powder diffraction analysis revealed the amorphous nature of these intermediates, even though, to facilitate crystallisation, the samples were held isothermally for 6 h.

Table 2
Chemical composition of the step I intermediates (145°C)

$Y(N_2H_3COO)_3$	Calculated/		Found/%	
	%	Ar	air	CO_2
N_2H_4	30.61	29.5	28.9	29.0
Y	28.31	28.8	28.8	30.3
CO_2	42.04	40.3	42.2	40.9

Greater differences between the thermoanalytical curves for different furnace atmospheres occur when the samples are heated to the final temperatures.

In an argon atmosphere, three additional steps in the thermal decomposition can be observed after dehydration. The chemical analysis of the intermediates and the end product is given in Table 3.

As could be expected, the high reactivity of the hydrazido part of the hydrazidocarbonate group and the endothermic nature of its formation make it more sensitive to thermal decomposition than are the other parts. Consequently the hydrazine content in the intermediates decreases rapidly with increasing temperature. Its content drops from the initial 26.2% to 3.2% in the intermediate obtained at 432°C.

Besides decomposition of the constituents of the sample and evolution of ammonia, carbon dioxide, nitrogen and/or carbon monoxide and hydrogen, other complex decompositions, transformations and recombinations of the hydrazidocarbonato group fragments also take place. This was confirmed by the chemical analysis of the intermediate, which revealed 8.9% of cyanate. The exact reaction schemes of these complex or even parallel reactions cannot be resolved on the basis of these sparse data, and the amorphous nature of the samples precludes any insight into the composition of the intermediate by X-ray diffraction.

The hydrazine content drops to zero at 708°C. The composition of the intermediate further changes and, in addition to the components previously present, cyanide was also detected, although in the minor content of 1.5%. The decomposition was accompanied by the evolution of carbon dioxide and nitrogen or carbon monoxide or both. The interplanar spacings and relative intensities were obtained (Table 4), and the crystallinity of the sample enabled the determination of the unit cell by X-ray diffraction. The obtained reflection maxima can be indexed by a primitive hexagonal

Table 3
Chemical analysis of the intermediates and the end product

Temperature of isolation/°C	Weight loss/%			Analysis/%		
		N_2H_4	Y	CN^-	CNO^-	C
432	52.1	3.2	49.9		8.9	
708	65.6		70.9	1.5	6.8	
1013	67.6		72.0			4.4
1300	69.3		69.9			5.5

Table 4
Observed and calculated interplanar *d*-spacings for intermediate obtained at 708°C

h	k	l	*d*(found)	*d*(calc.)	I/I_0
0	0	1	8.2067	8.1756	52
0	0	2	4.0972	4.0878	27
1	0	0	3.1932	3.2053	31
1	0	1	2.9843	2.9841	100
0	0	3	2.7295	2.7252	52
1	0	2	2.5238	2.5223	21
1	0	3	2.0772	2.0762	34
1	1	0	1.8518	1.8505	69
0	0	4	–	2.0420	unobserved[a]
1	1	1	1.8068	1.8049	18
1	0	4	1.7217	1.7233	9
1	1	2	1.6853	1.6858	21
0	0	5	1.6340	1.6351	7
2	0	0	1.6027	1.6026	11
2	0	1	1.5723	1.5727	17
1	1	3	1.5321	1.5310	38
2	0	2	1.4911	1.4921	10
1	0	5	1.4566	1.4565	8

[a] Very low intensity or overlapping with previous reflection.

unit cell with parameters $a = 3.701(2)$, $c = 8.176(4)$. This finding confirms that this intermediate is not a mixture of compounds but a single phase. The data do not fully correlate with any of the data in the PDF-2 database [14], although the presence of traces of yttrium oxide can be presumed.

In addition to the bands at 313(m), 443(vs), 488(sh) and 656(s), the IR spectra also exhibit very strong bands at 2130 cm^{-1}. This band wave number is in accordance with the presence of cyanate or another group with a triple bond. In this region hydride vibrations can be also expected, but in the similar case of the thermal decomposition of deuterated cobalt hydrazidocarbonate [15] this possibility was excluded.

The decomposition of the intermediate proceeds further up to the final temperature of 1300°C. In this step the sample looses an additional 4.3% of its weight. No evolution of gases was detected by EGA, possibly because of the dilution of the gaseous sample by the purge gas and the high background and lower limit of detection of the apparatus. In X-ray analysis, the presence of the high temperature form of yttrium oxide (PDF 41-1105) corresponding to the C type of rare earth oxides was determined.

At this temperature, it was observed that a black material is also present in the residue. In an experiment, the intermediate that was isolated at 1013°C in an argon atmosphere was also black. The appearance of the sample suggested the presence of solid carbon. This was confirmed by thermogravimetric measurements in air, when the carbon oxidised and a weight loss of 4.2% was obtained. The chemical analysis of the residue isolated at 1013 and 1300°C showed 4.4% and 5.5% of elementary carbon respectively.

Thermal decomposition of yttrium hydrazidocarbonate trihydrate in air proceeds in three steps, as shown in Fig. 3 and Table 1.

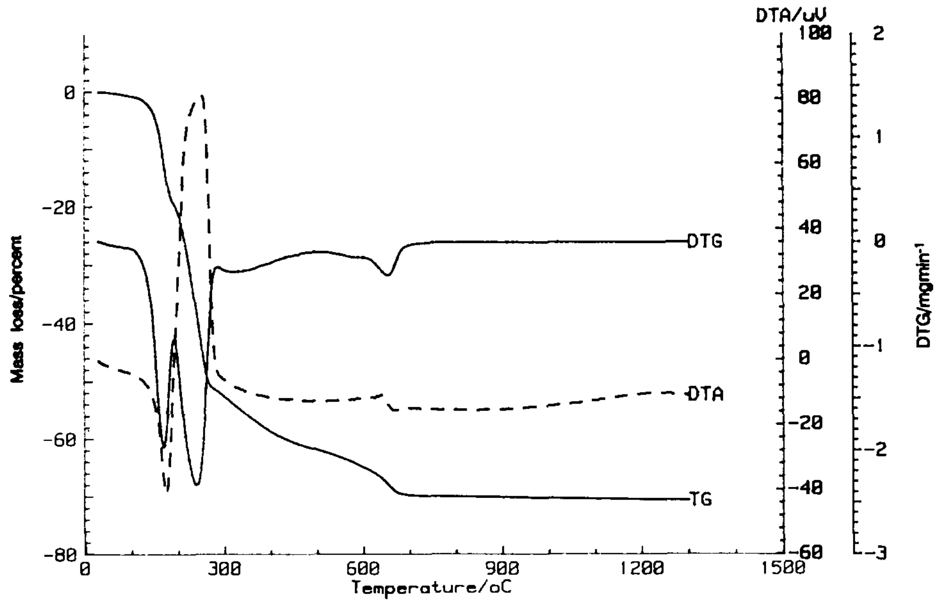

Fig. 3. TG/DTG/DTA curves of $Y(N_2H_3COO)_3 \cdot 3\,H_2O$ in air.

Thermal decomposition of the sample in air proceeds in a manner unlike that in argon. The dehydration step has already been discussed collectively for all three atmospheres. Thermoanalytical curves reveal another two steps in the decomposition (Fig. 2). The final product obtained at 708°C is the high temperature C form of yttrium oxide (PDF 41-1105), which contains 75.7% of Y (the calculated Y content in Y_2O_3 is 78.74%).

Because of the potential use of the starting compound as a precursor for the preparation of reactive yttrium oxide, measurements of the particulate properties were made. These samples were prepared: (a) by the standard temperature programme as described before but with prolonged isothermal heating (6 h) at the final temperature, and (b) by heating the sample at $20\,K\,min^{-1}$ to the final temperature without an isothermal period. The crystallite size, as obtained from XRD measurements, for the product isolated under the (a) conditions was 0.014 μm, $d_{50} = 1.53$ μm and surface area $13.4\,m^2\,g^{-1}$. Under the (b) conditions the crystallite size was 0.010 μm, $d_{50} = 1.68$ μm and surface area $36.5\,m^2\,g^{-1}$. The product is in the shape of needle-like crystals. The shape of the crystals makes the determination with laser diffraction apparatus less reliable, and therefore scanning electron micrographs were used.

Thermal decomposition in carbon dioxide at lower temperatures proceeds similar to that in an argon atmosphere (Fig. 4). Carbon dioxide in this temperature interval does not notably influence the decomposition. Because of its presence in the hydrazidocarbonate group, one might assume so for equilibrium conditions.

In carbon dioxide the last stage of thermal decomposition occurs at high temperature and the sole residue is yttrium oxide. Chemical analysis indicates it to be very pure

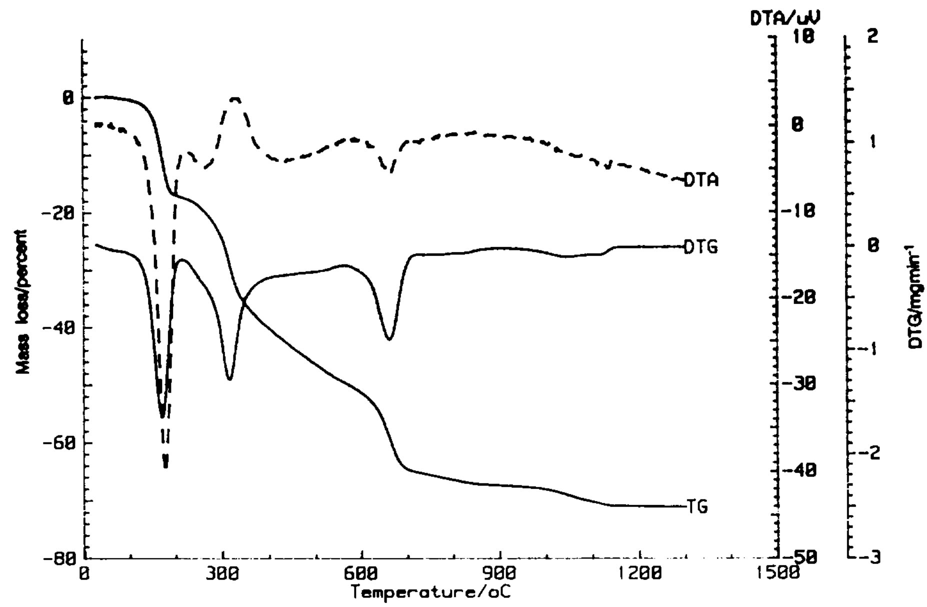

Fig. 4. TG/DTG/DTA curves of $Y(N_2H_3COO)_3 \cdot 3H_2O$ in carbon dioxide.

Y_2O_3 (Y content 78.7%). By X-ray analysis only yttrium oxide was detected (PDF 41-1105). This is also in accordance with the IR spectra of the sample. The IR bands observed at 308, 342, 471 and 562 cm^{-1} (the first two being very sharp) are characteristic for this type of oxide and are in accordance with published data [16]. The presence of solid carbon was not observed in the final residue, unlike the case for the argon atmosphere, because carbon reacts with the carrier gas in accordance with the Boudouards equilibrium

$$CO_2 + C \rightleftharpoons 2CO$$

4. Conclusions

Yttrium hydrazidocarbonate trihydrate undergoes substantial weight loss during heating, owing to the high volatility of the decomposition products of the anion, e.g. the hydrazidocarbonato ion. The first step in all three atmospheres, argon, air and carbon dioxide, is the dehydration of the sample leading to the anhydrous compound, but with some hydrolysis.

The furnace atmosphere affects the decomposition more at higher temperatures, leading to greater differences between the courses of decomposition in argon and carbon dioxide as compared with air. The final product in all three atmospheres is the high temperature C form of Y_2O_3. The atmosphere and the heating programme influence the characteristics of the end product. In argon, amorphous solid carbon is also observed in the final residue. The oxide obtained is very pure and of the same high temperature C form in air and carbon dioxide atmospheres. On the other hand, the oxidative atmosphere air greatly influences the final temperature of the decomposition. The surface area and other particulate properties are substantially dependent on the heating rate and final temperature, e.g. the parameters that affect the sintering of the sample.

Acknowledgements

The authors express their grateful thanks to B. Sedej for the chemical analyses and to Dr. A. Meden for the powder diffraction analysis.

References

[1] M. M. Amala Sekar and K.C. Patil, Mater. Res. Bull., 28 (1993) 485.
[2] P. Ravindranathan and K.C. Patil, J. Mater. Sci., 22 (1987) 3261.
[3] J. Maček, R. Hrovat and B. Novosel, J. Therm. Anal., 40 (1993) 335.
[4] M. M. Amala Sekar, S. S. Manoharan and K.C. Patil, J. Mater. Sci. Lett., 9 (1990) 1205.
[5] J. Slivnik and A. Rihar, Monatsh. Chem., 103 (1972) 1572.
[6] W.R. McBride, R.A. Henry and S. Skolnik, Anal. Chem., 23 (1951) 890.
[7] A.I. Busev, V.G. Tiptsova and V.M. Ivanov, Handbook of Analytical Chemistry of Rare Elements, Ann Arbor-Humphrey Science Publishers, London, 1970.
[8] R. Pribil, Applied Complexometry, Pergamon Press, Oxford, 1980.
[9] A.I. Vogel, Textbook of Quantitative Inorganic Analysis, Longmans, London, 1978.
[10] W. Fresenius and G. Jander, Handbuch der analytischen Chemie, 3. Teil, Bd. IVa, Elemente der vierten Hauptgruppe I, Springer-Verlag, Berlin, 1967.
[11] APHA, AWWA, WPCF, Standard Methods for the Examination of Water and Waste Water, 14th Edn., Washington, DC, 1975.
[12] J. Maček and A. Rahten, Thermochim. Acta, 224 (1993) 217.
[13] A. Braibanti, A. Tiripicchio, A.M. Manotti Lanfredi and M. Camellini, Acta Crystallogr., 23 (1967) 248.
[14] The Powder Diffraction File, Sets 1–43, JCPDS ICDD, Newtown Square, USA, 1993.
[15] R. Hrovat, M.Sc. Thesis, University of Ljubljana, Dept. of Chemistry and Chem. Technology, Ljubljana 1991.
[16] W.B. White and V.G. Keramidas, Spectrochim. Acta, Part A, 28A (1972) 501.