Thermal behaviour of the basic carbonates of lanthanum–europium

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Abstract

The basic carbonates of lanthanum with 10%, 20%, 50% and 80% of europium were prepared by precipitation from homogeneous solutions via the hydrolysis of urea, without the addition of an auxiliary anion, at two different temperatures. Elemental analysis, complexometric methods, X-ray diffraction patterns, solid state IR absorption, thermogravimetry/derivative thermogravimetry (TG/DTG) and differential thermal analysis (DTA) were used to characterise the compounds and study their thermal behaviour.

Keywords: Basic carbonate; Decomposition; Europium; Homogeneous precipitation; Lanthanum; TA

1. Introduction

Several methods of preparation of hydrated basic carbonates of lanthanide and yttrium, as well as studies of their thermal behaviour, have been carried out [1–6]. However, very few works have described the thermal behaviour of these compounds after preparation by precipitation from homogeneous solutions via hydrolysis of urea, without the addition of any auxiliary anion [5,6].

Over the last few years, interest in the preparation of the basic carbonates of lanthanide via the hydrolysis of urea has increased considerably, since the technique

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allows one to obtain monodisperse particles, the size and form of which can be controlled [7–9].

The present work investigates the influence of preparation method, i.e. precipitation from homogeneous solution via the hydrolysis of urea, without addition of auxiliary anions, on the thermal decomposition of europium and lanthanum in the basic carbonates of lanthanum and europium, at two different temperatures. This paper is an extension of the research work undertaken previously by D'Assunção and co-workers [5,6].

2. Experimental

Mixtures of lanthanum oxide with 10%, 20%, 50% and 80% (mol/mol) of europium oxide were dissolved in hot concentrated hydrochloric acid and evaporated to eliminate excess acid. Lanthanide chloride solutions of concentration approx. 6.0×10^{-3} mol l^{-1} containing urea, 0.54 mol l^{-1}, were heated at two different temperatures. For a fast precipitation, the solutions were boiled for 90 min after the precipitation had begun, and thereafter left standing for 24 h. For a slow precipitation, the solutions were heated at approximately 85°C for 90 min after the precipitation had begun, and then left standing for 24 h. The precipitates were washed with distilled water until the chloride ions had been completely eliminated, in accordance with earlier procedures [5].

The total amounts of lanthanum and europium ions were determined by complexometric titration with standard EDTA solutions, using xilenol orange as indicator [10].

Carbon and hydrogen were determined by microanalytical procedures using a Perkin-Elmer elemental analyser.

In order to obtain the general formula, the amounts of lanthanum and europium were calculated from the proportions of the respective oxides used. The amount of carbonate was determined by elemental analysis and hydroxyl ion concentrations were calculated in order to satisfy neutrality conditions. The amount of water was obtained by elemental analysis after the quantity of hydroxyl ions had been subtracted.

Diffraction patterns were obtained with an HZG 4/B horizontal diffractometer (G.D.R.), using Cu Kα radiation ($\lambda = 1.541$ Å).

The solid state IR absorption spectra were obtained in a Perkin-Elmer FT-IR spectrophotometer model 1750, using KBr pellets.

The TG/DTG curves were obtained using a Mettler TA-4000 thermoanalyser system with an air flow of 40 ml min^{-1} and heating rate of 10°C min^{-1}, and with samples weighing about 8 mg. An alumina crucible was used for the TG/DTG curves.

The DTA curves were obtained using a Perkin-Elmer DTA 1700 apparatus and α-alumina as the reference material. Samples of about 8 mg were put in the alumina crucible and heated at a rate of 20°C min^{-1} in an air flow of 40 ml min^{-1}.

Table 1
Analytical and microanalytical results

| Compound		Total amount of lanthanide in %		Carbon/in %		Hydrogen/in %		General formulation $La_a Eu_b (OH)_c (CO_3)_d \cdot xH_2O$				
		Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	a	b	c	d	x
La:Eu (90:10)	f,s	62.49	62.56	5.89	5.75	0.59	0.58	1.81	0.19	1.60	2.20	0.50
La:Eu (80:20)	f	63.06	63.00	5.62	5.70	0.41	0.46	1.62	0.38	1.80	2.10	0.50
La:Eu (80:20)	s	58.00	56.08	5.96	5.86	1.08	1.48	1.62	0.38	1.20	2.40	3.00
La:Eu (50:50)	f	62.44	62.97	5.42	5.45	0.83	0.83	1.04	0.96	1.80	2.10	1.00
La:Eu (50:50)	s	57.06	57.02	5.66	5.59	1.43	1.47	1.04	0.96	1.20	2.40	3.00
La:Eu (20:80)	f	63.77	63.48	4.88	4.86	0.91	1.05	0.43	1.57	2.20	1.90	1.00
La:Eu (20:80)	s	58.45	58.73	5.88	5.86	1.19	1.22	0.43	1.57	1.00	2.50	2.50

Key: f, fast precipitation; s, slow precipitation.
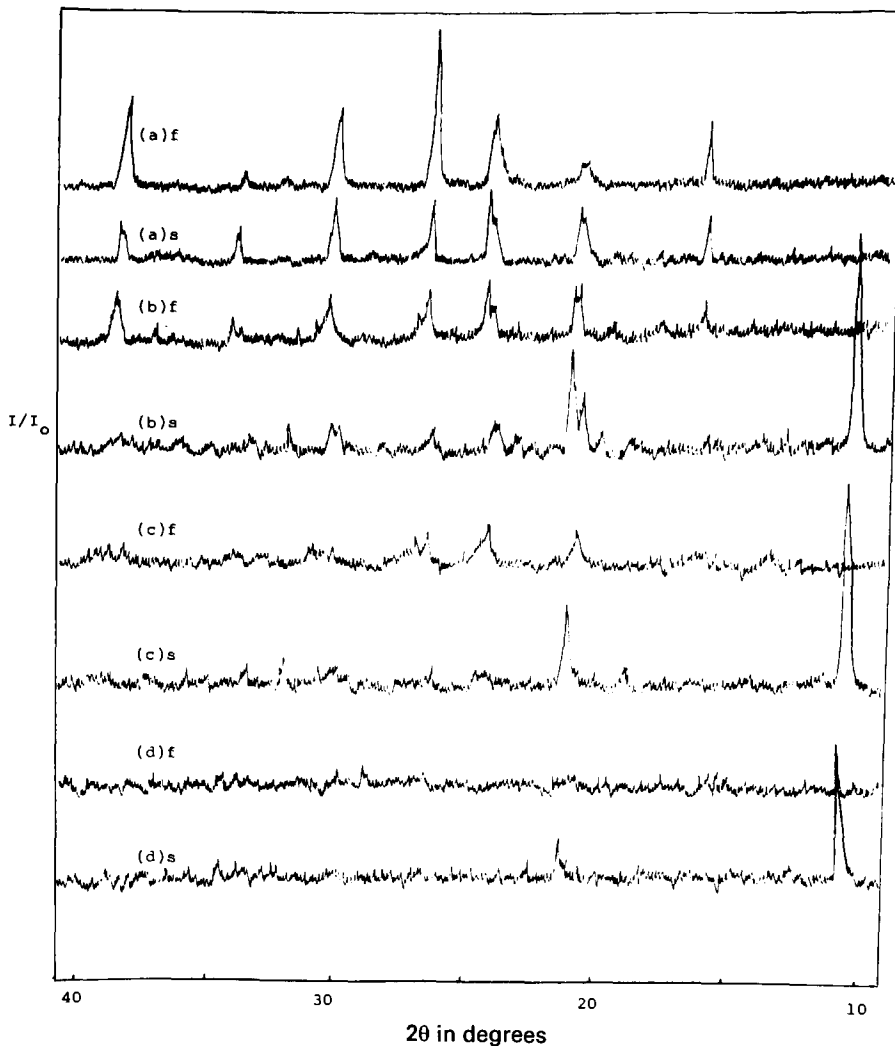
Fig. 1. X-ray powder patterns of the basic carbonates of: (a) La:Eu (90:10); (b) La:Eu (80:20); (c) La:Eu (50:50) and (d) La:Eu (20:80). f = fast precipitation, s = slow precipitation.

3. Results and discussion

Table 1 presents analytical data for the compounds prepared. The results show evidence of the increase in the molar ratio of compound: hydroxyl ion for the fast precipitation, owing to the rapid hydrolysis of the urea, with a rapid pH increase.

The X-ray powder diffraction patterns (Fig. 1) show that the compounds have a crystalline structure, except for the compound of La : Eu = 20 : 80 obtained by fast
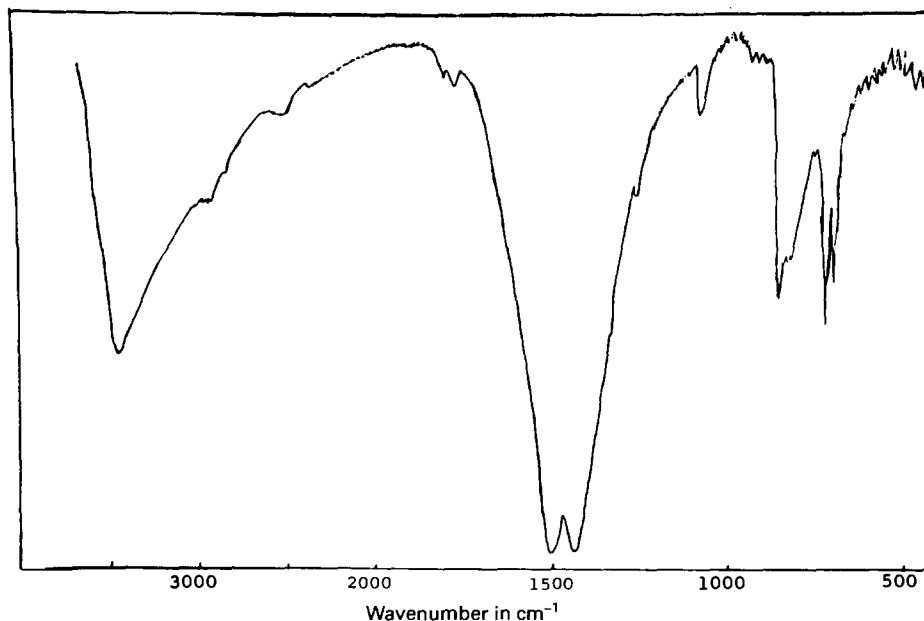
Fig. 2. Infrared absorption spectra between 4000 and 500 cm^{-1} of the basic carbonate of La:Eu (50:50) obtained by fast precipitation.

precipitation. For the other compounds, the X-ray powder diffractions show that the compounds precipitated by the slow process have a higher degree of crystallinity than those precipitated by the fast process. The X-ray diffraction patterns also show that for the same compound, precipitation by the slow or fast process results in significant differences, as can be seen in Fig. 1.

Fig. 2 shows the IR spectra between 4000 and 500 cm^{-1} for the compound with La:Eu = 50:50, obtained by fast precipitation as representative of all compounds. The broad and strong absorption bands between 3700 and 3000 cm^{-1} are ascribed to water and hydroxyl ion vibration modes. The strong bands between 1500 and 1400 cm^{-1}, and bands of medium intensity between 1100 and 700 cm^{-1} are attributed to carbonate ions. These interpretations are in agreement with the data of Refs. [5] and [11].

The TG/DTG curves are shown in Figs. 3 and 4. The curves show mass losses between 30 and 850°C, and the results have been found to be characteristic for each compound. Only for the compound with La:Eu = 80:20, obtained by fast and slow precipitation, do the TG/DTG curves show significant differences in the thermal decomposition observed between 400 and 600°C. For the other compounds no significant difference is observed. The influence of the concentration of each lanthanide ion on the thermal decomposition can also be seen. For the compounds with La:Eu = 90:10 (fast and slow precipitation) and La:Eu = 80:20 (fast precipitation), the TG/DTG curves are similar to those for
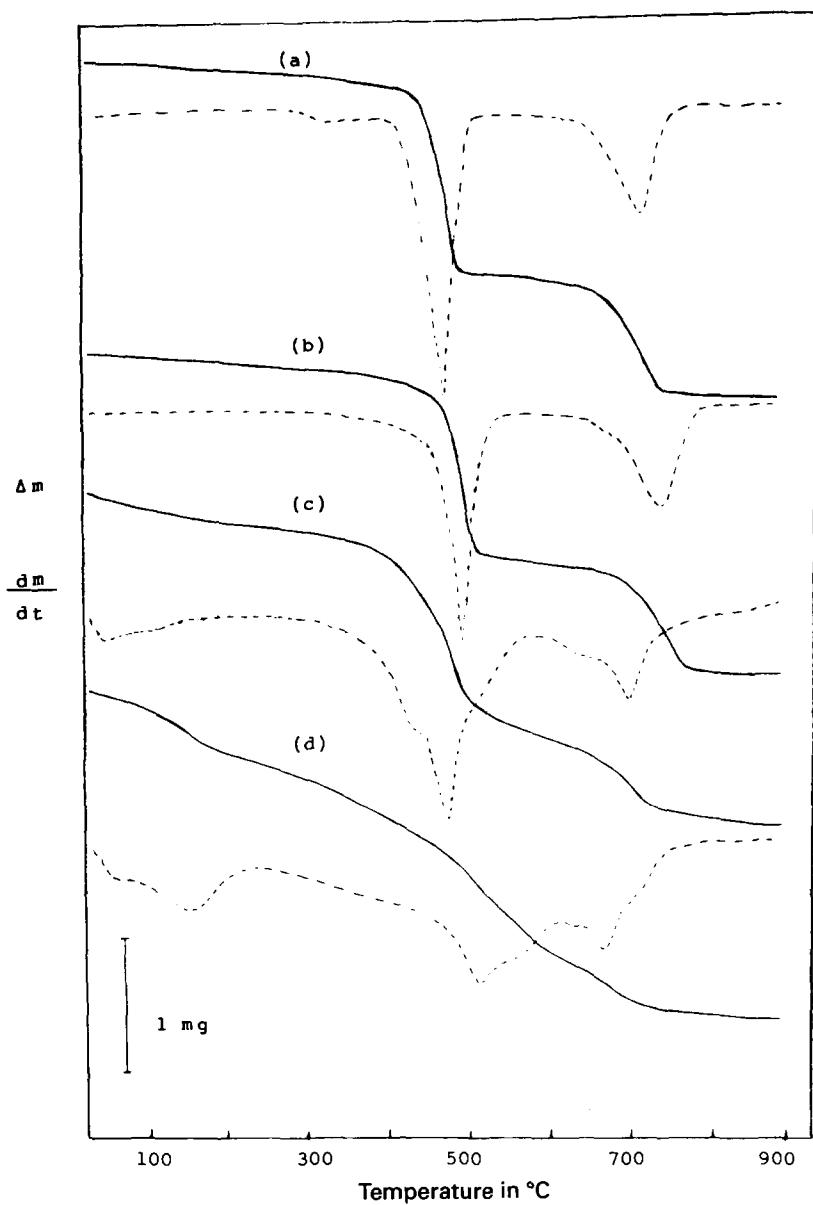
Fig. 3. TG/DTG curves of the basic carbonates of: (a) La:Eu (90:10); (b) La:Eu (80:20); (c) La:Eu (50:50) and (d) La:Eu (20:80), obtained by fast precipitation.

hydrated basic lanthanum carbonate [5]. The compounds with La : Eu = 80 : 20 (slow precipitation) and La : Eu = 50 : 50 (fast and slow precipitation) show typical thermal behaviour.
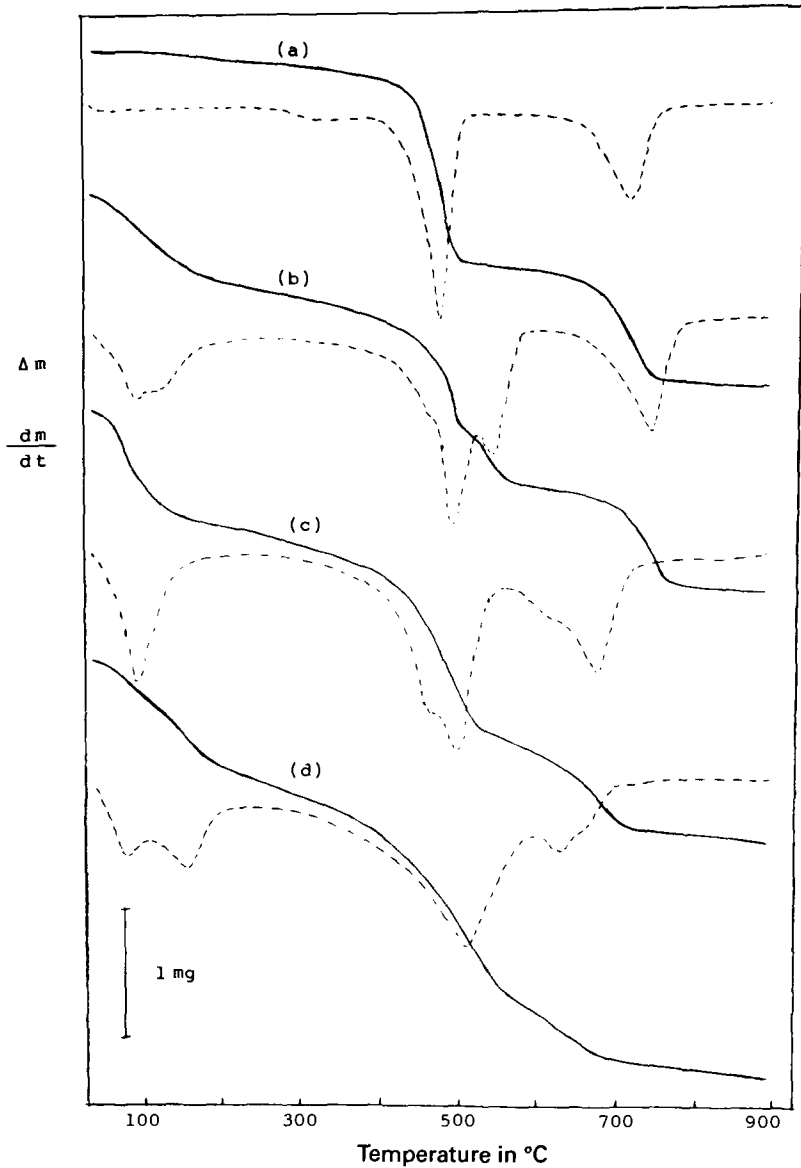
Fig. 4. TG/DTG curves of the basic carbonates of: (a) La:Eu (90:10); (b) La:Eu (80:20); (c) La:Eu (50:50) and (d) La:Eu (20:80), obtained by fast precipitation.

The thermal decomposition shows that, except for the compound with La : Eu = 20 : 80, initial mass loss occurs over 500°C. This behaviour is explained by the elimination of water, hydroxyl ions and CO_2, with formation of an intermediate whose stoichiometry is close to $Ln_2O_2CO_3$. The last mass loss between 500 and 850°C is due to the final thermal decomposition with formation of the respective

Table 2
Temperature range and mass loss for the hydrated basic carbonates

Sample			Initial mass in mg	Temperature range in °C	% mass loss	Δm in mg	Attribution
La:Eu	10%	f	8.035	30–294	0.26	0.021	$0.1H_2O$
				294–500	17.03	1.369	$1.2CO_2 + 1.2H_2O$
				628–760	9.87	0.793	$1.0CO_2$
La:Eu	10%	s	8.045	30–294	0.49	0.035	$0.1H_2O$
				294–498	16.79	1.351	$1.2CO_2 + 1.3H_2O$
				630–748	9.90	0.797	$1.0CO_2$
La:Eu	20%	f	8.038	30–316	0.71	0.057	$0.2H_2O$
				316–540	15.97	1.284	$1.2CO_2 + 1.2H_2O$
				640–786	9.51	0.764	$1.0CO_2$
La:Eu	20%	s	8.052	30–220	8.47	0.682	$2.5H_2O$
				220–576	17.08	1.395	$1.5CO_2 + 1.1H_2O$
				640–770	8.49	0.684	$1.0CO_2$
La:Eu	50%	f	8.051	30–330	2.89	0.233	$1.0H_2O$
				330–550	16.03	1.290	$1.0CO_2 + 1.0H_2O$
				550–840	7.76	0.625	$0.8CO_2$
La:Eu	50%	s	8.045	30–190	9.15	0.734	$2.5H_2O$
				190–530	16.92	1.361	$1.5CO_2 + 1.2H_2O$
				530–730	7.67	0.617	$0.9CO_2$
La:Eu	80%	f	8.013	30–800	26.86	2.152	$2.0H_2O + 2.0CO_2$
La:Eu	80%	s	8.029	30–770	32.13	2.580	$3.0H_2O + 2.6CO_2$

Key; f, fast precipitation; s, slow precipitation.

oxides, Ln_2O_3. For the compound with La:Eu = 20:80, the thermal decomposition occurs via a consecutive mass loss between 30 and 850°C, with formation of the respective oxide Ln_2O_3, without stable intermediate formation. The temperature ranges and mass losses for the hydrated basic carbonates are shown in Table 2.

The DTA curves are given in Fig. 5. They show endothermic peaks, most of them corresponding to the mass losses observed in the TG/DTG curves.

4. Conclusions

The composition and degree of crystallinity of the hydrated basic carbonates of lanthanum–europium are affected by the precipitation temperature. The TG/DTG curves are characteristic of each compound. Except for the compound with La:Eu = 20:80 (fast and slow precipitation), the TG/DTG curves show the formation of an intermediate with a composition close to $(LnLn')_2O_2CO_3$. For the compound with La:Eu = 20:80, thermal decomposition occurs via a consecutive
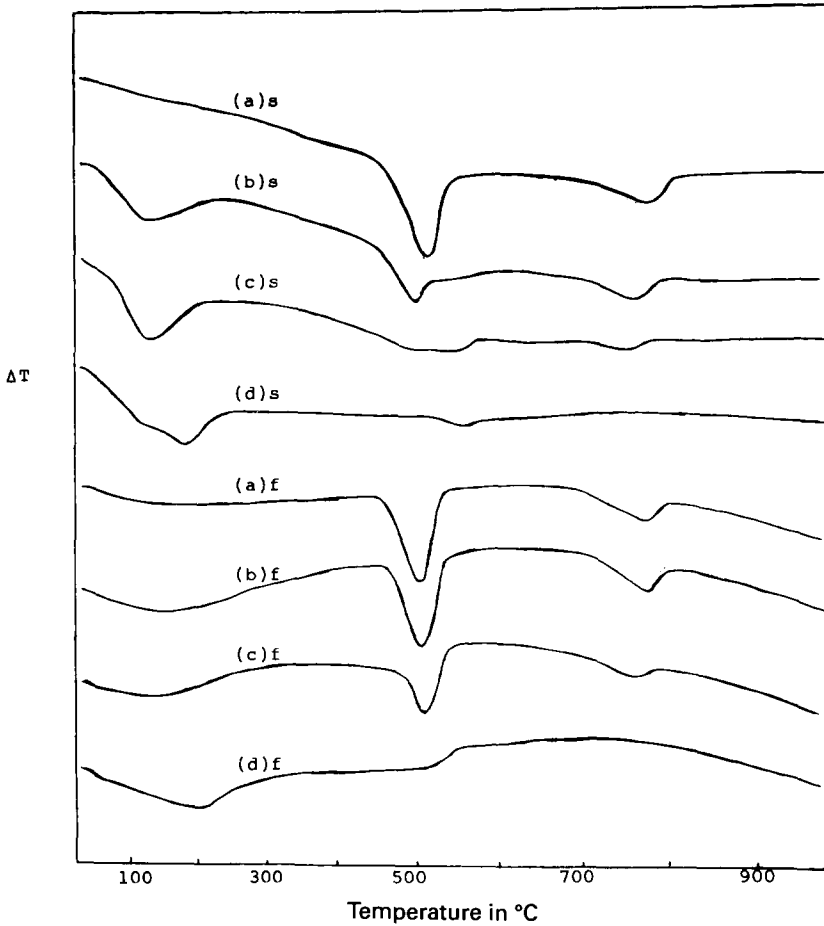
Fig. 5. DTA curves of the basic carbonates of: (a) La:Eu (90:10); (b) La:Eu (80:20); (c) La:Eu (50:50) and (d) La:Eu (20:80). s = slow precipitation, f = fast precipitation.

mass loss, with formation of the respective oxide $(LnLn')_2O_3$, and without formation of a stable intermediate. The DTA curves show endothermic peaks corresponding to the mass losses observed in the TG/DTG curves.

On increasing the Eu^{3+} concentration, the onset of the first CO_2 loss shifts to a higher temperature, while a temperature decrease accompanies the last CO_2 loss.

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