

Synthesis of Hydrated Lutetium Carbonate

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Crystalline lutetium carbonate was synthesized from the corresponding chloride using ammonium bicarbonate as precipitant. The chemical analyses suggest that the synthesized lutetium carbonate is a hydrated basic carbonate or oxycarbonate. The X-ray powder diffraction data are presented. The IR data for the compound show the presence of two different carbonate groups. There is no stable intermediate carbonate in the process of thermal decomposition of the lutetium carbonate.

Carbonates of rare earths of various compositions have been reported as a result of numerous syntheses and thermal analyses.^{1–12} Many of the results reported and accompanying discussions concerning their compositions and properties are contradictory, however. The inconsistencies are partly due to preparatory difficulties and to a lack of structural data.

Caro *et al.*⁴ obtained $\text{Lu}_2(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$ by vigorously stirring a water suspension of the powered oxide in a CO_2 atmosphere. This compound, however, appears amorphous as viewed by its X-ray diffraction pattern.

The most convenient method for the preparation of rare-earth carbonates is by precipitating the compounds using alkali carbonates or bicarbonates from a solution containing the metal salt. In this way a crystalline lutetium carbonate has been obtained when using ammonium bicarbonate as precipitant. The product has been characterized by X-ray powder diffraction and IR methods.

Experimental

To 10 ml of 0.5 M lutetium chloride in water was added 1.0 g of ammonium bicarbonate at 25 °C. The solution was maintained at 25 °C for one week. The precipitate was then filtered off, washed repeatedly with water, air-dried and subjected to analysis. The yield was 84.3%.

The lutetium chloride solution was checked for Lu^{3+} content by EDTA titration. Lutetium carbonate was analyzed by combustion analysis (CO_2 and H_2O) and also by ignition of lutetium carbonate in the air to Lu_2O_3 .

The X-ray powder diffraction pattern was obtained using a Siemens D500 X-ray diffractometer with $\text{Cu K}\alpha$ radiation with a scan rate of 4° min^{-1} ; the error in

measuring the diffraction angle was 0.001° . The IR absorption spectrum was recorded using a FTIR-740IR spectrophotometer and a KBr disc. The thermal decomposition process of lutetium carbonate was investigated with a Dupont 9900 thermal analyzer using 10 mg samples in shallow platinum crucibles which were heated in air at a heating rate of $10^\circ \text{C min}^{-1}$. Precipitate morphology was assessed from a micrograph taken with a JSM-35 scanning electron microscope.

Results and discussion

The results of the chemical analyses of lutetium carbonate was: $\text{Lu}_2\text{O}_3 : \text{CO}_2 : \text{H}_2\text{O} = 1.00 : 2.01 : 6.35$. This suggests that the synthesized lutetium carbonate is a hydrated basic carbonate or oxycarbonate. The molar ratios, $\text{Lu}_2\text{O}_3 : \text{CO}_2 (: \text{H}_2\text{O})$ are not whole numbers. This apparent anomaly may be attributed to admixed amorphous particles and to the instability of the carbonates.³

Figure 1 shows a micrograph of the precipitate

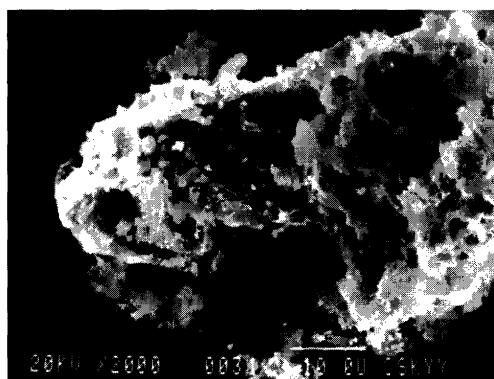


Fig. 1. Micrograph of lutetium carbonate ($\times 2000$).

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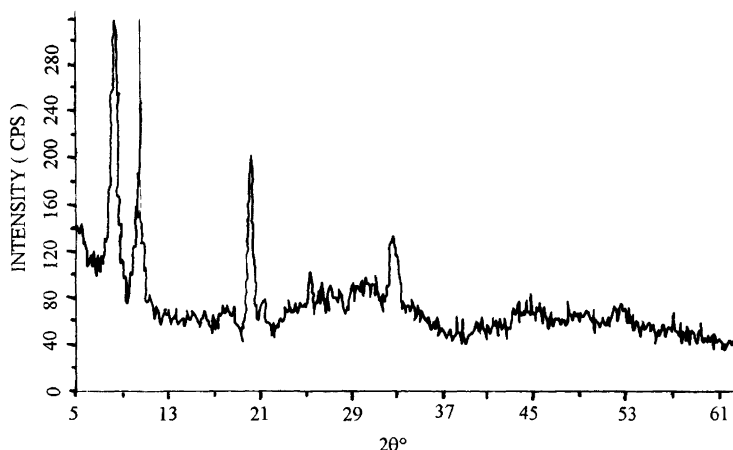


Fig. 2. X-ray powder diffraction pattern of lutetium carbonate.

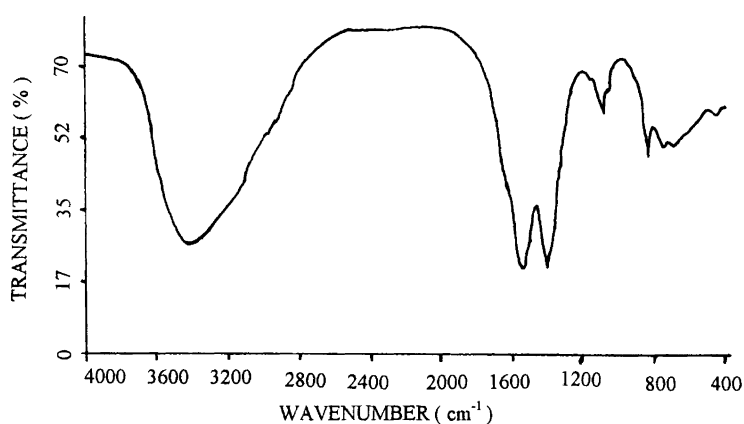


Fig. 3. IR spectrum of lutetium carbonate.

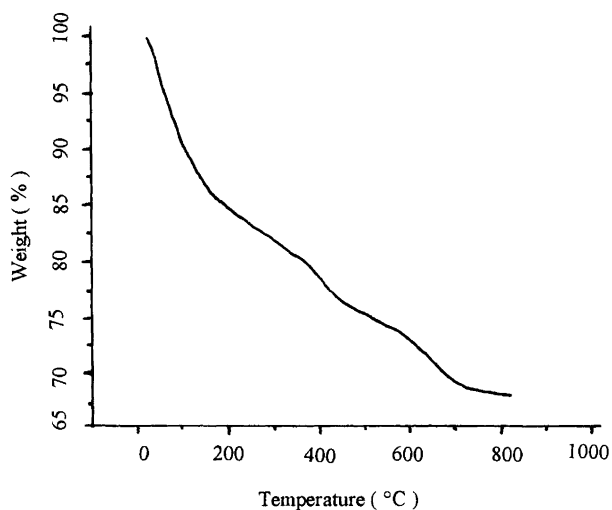


Fig. 4. TG curve of lutetium carbonate.

indicating the presence of plate-shaped crystals mixed with a large number of small particles. The X-ray powder diffraction pattern and powder data of the carbonate are shown in Fig. 2 and Table 1, respectively. As far as we know from the literature, this is the first report of X-ray powder data for a hydrated lutetium carbonate.

Table 1. X-Ray diffraction data for lutetium carbonate.

$d/\text{Å}$	I/I_0
10.5716	93.7
8.4064	100
8.1697	37.9
4.3899	59.7
4.1725	23.8
3.5037	31.1
2.7334	38.3

Herberg¹³ gave the frequencies for the four modes of the free carbonate ion: 1063 cm^{-1} ; 879 cm^{-1} ; 1415 cm^{-1} ; 680 cm^{-1} , when the first two modes were non-degenerate. The splitting of the non-degenerate bands is generally an indication of nonequivalent carbonate groups in a given structure.¹⁴

The IR spectrum is shown in Fig. 3 and the results are given in Table 2. The notation of the absorption bands is given according to Fujita.¹⁵ Since there are more than six normal vibrational bands for the carbonate group and the non-degenerate γ_2 is distinctly split, there must be two nonequivalent carbonate groups (bidentate and unidentate) in the unit cell.

Table 2. IR spectrum (all bands in cm^{-1}) of lutetium carbonate (Fujita notation).

γ_5	γ_1	γ_2	γ_8	γ_3	γ_6	Additional bands
1544	1394	1084 1045	840	756	693	3507 (H_2O) 1622 (HOH bending)

The thermogravimetric curve (TG) for lutetium carbonate is shown in Fig. 4. The thermal decomposition of lutetium carbonate contains dehydration and decarbonation processes. There is no evidence for the formation of any stable intermediate carbonates, and the end product is Lu_2O_3 .

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