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Synthesis and Characterization of Hydrated Holmium and Erbium Carbonates

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Crystalline hydrated holmium and erbium carbonates were synthesized using ammonium bicarbonate as precipitant. The holmium and erbium carbonates prepared are hydrated normal carbonates and the structure and properties were investigated by XRD, SEM, TG and IR techniques. The holmium and erbium carbonates consist of spherical aggregates of crystallites. The structures are closely related to those of tengerite type rare earth carbonates in the literature. The IR data for the holmium and erbium carbonates show the presence of two different carbonate groups (bidentate and unidentate carbonates) in the unit cell. In the process of thermal decomposition of the holmium and erbium carbonates to oxide, no stable intermediate was detected.

Key Words: Holmium carbonate, Erbium carbonate, Crystal, Ammonium bicarbonate.

INTRODUCTION

Rare earth carbonates of various compositions have been reported as a result of numerous syntheses and thermal analyses[1-13]. Many reported results and discussions concerning their compositions and properties are contradictory. The inconsistencies are due, in part, to preparative difficulties and to lack of structural data. That is to say, crystalline carbonates of rare earth elements are not easy to synthesize.

Caro *et al.*[1] obtained $Ho_2(CO_3)_3\cdot 2\sim 3H_2O$ and $Er_2(CO_3)_3\cdot 2\sim 3H_2O$ by vigorously stirring a water suspension of holmium and erbium oxide powders under a CO_2 atmosphere, Christensen and Hazell[2] prepared $Ho_2(OH)_4CO_3$ and $Er_2\ (OH)_4CO_3$ by hydrothermal technique. Charles[3] obtained $Ho_2(CO_3)_3\cdot 2H_2O$ and $Er(CO_3)_{1.23}(OH)_{0.54}\cdot 1.7H_2O$ by the hydrolysis of holmium and erbium trichloroacetates.

The most convenient method for the preparation of rare earth carbonates is the precipitation by alkali carbonates or bicarbonates from solutions

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containing the metal salt. Ammonium bicarbonate has been found to be a good precipitant[14-20]. Previously, the synthesis and structure of hydrated europium, terbium, neodymium, lutetium, yttrium, ytterbium and cerous carbonates are reported[14-20]. In this paper, the synthesis of crystalline holmium and erbium carbonates using ammonium bicarbonate as precipitant is investigated. The products are characterized by X-ray powder diffraction and IR methods.

EXPERIMENTAL

To constantly-stirred 50 mL of 0.1 M rare earth (holmium and erbium) chloride solution contained in a beaker, was added 50 mL 0.3 M aqueous ammonium bicarbonate at 25ºC. The precipitate appeared and gas bubbles sent up rapidly. The solution was maintained at 25ºC for 1 week. The resulting precipitate was then filtered, washed with water repeatedly, air-dried and subjected to analysis.

Rare earth carbonate was analyzed by combustion analysis (CO_2 and H_2O) and also by ignition of rare earth carbonate in air to RE_2O_3.

X-ray powder diffraction patterns were obtained using a RAX-10 X-ray diffractometer and CuKα radiation with a scan rate of 4°/min. The IR absorption spectrum was recorded using a FTIR-740 IR spectrophotometer and KBr pellets. The thermal decomposition process of rare earth carbonate was investigated with a Dupont 9900 thermalanalyzer, using 10 mg samples in shallow platinum crucibles which were heated in air at a heating rate of 10ºC/min. The morphology of the precipitate was assessed by micrographs taken with a JSM-35 scanning electron microscope.

RESULTS AND DISCUSSION

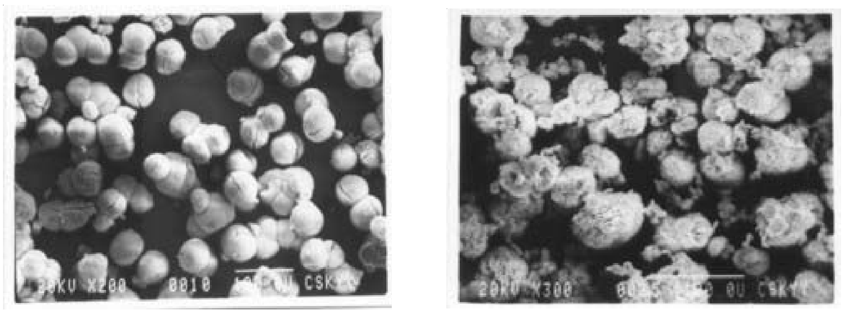
The results of the chemical analyses of holmium and erbium carbonate are:

Ho_2O_3: CO_2: H_2O = 1.00:2.85:3.37

Er_2O_3: CO_2: H_2O = 1.00:2.81:3.21

These suggest that holmium and erbium carbonates synthesized are hydrated normal carbonates. The molar ratios Re: H_2O are not a whole number. The apparent anomaly may be attributed to the instability of the carbonate[8]. Concerning the instability of rare earth carbonates, Shinn and Eick[4] mentioned two bonding positions of carbonate ions in the lanthanide structure, one coordinates as a unidentate ligand and one as a bidentate ligand. Water molecules behave similarity; one coordinates to a metal ion and one does not, therefore some of carbonate ions and water molecules may be expected to be rather easily lost from the structure.

Fig. 1 shows the micrographs of precipitated rare earth carbonates, which indicated the presence of spherical aggregates of crystallites.



(a) (b)

Fig. 1. Micrograph of holmium carbonate (a) and erbium carbonate (b)

The X-ray powder diffraction pattern and diffraction data of the rare earth carbonate are shown in Fig. 2 and Table-1, respectively. The data correspond to those of tengerite type rare earth carbonate[1,6, 7].

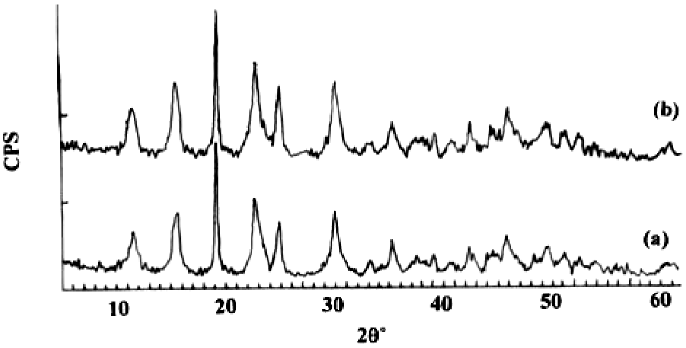


Fig. 2. X-ray diffraction patterns of holmium carbonate (a) and erbium carbonate (b)

TABLE-1
X-RAY DIFFRACTION DATA FOR HOLMIUM AND ERBIUM CARBONATES

Holmium carbonate	d(nm)	0.7613	0.5655	0.4598	0.3890	0.3554	0.2964	0.2535	0.2127	0.1973
	I/I_0	32	44	100	56	39	47	27	20	28
Erbium carbonate	d(nm)	0.7600	0.5650	0.4588	0.3869	0.3552	0.2957	0.2528	0.2118	0.1968
	I/I_0	32	52	100	66	50	53	25	24	32

Herberg[21] gave the infrared frequencies for the four modes of the free carbonate ion: 1063 cm^{-1}, 879 cm^{-1}, 1415 cm^{-1} and 680 cm^{-1}, when the first two modes non-degenerate. The splitting of the non-degenerate bands is generally an indication of nonequivalent carbonate groups in a given structure[22].

The IR spectra of the holmium and erbium carbonate are shown in Fig. 3 and the assignments are given in Table-2; the notation of absorption bands is according to Fujita[22]. The IR spectra of tengerite type rare earth carbonates are similar to those obtained in this work[1,6,7]. Since there are more than six normal vibrational bands for carbonate group and non-degenerate frequencies γ_2 and γ_8 are clearly split in the IR spectra obtained here, there must be two nonequivalent carbonate groups (bidentate and unidentate carbonates) in the unit cell[1].

TABLE-2
IR SPECTRAL BANDS (cm^{-1}) OF HOLMIUM AND ERBIUM CARBONATES (FUJITA NOTATION)

	ν_5	ν_1	ν_2	ν_8	ν_3	ν_6	Additional bands
Holmium carbonate	1511	1452 1423	1090 1050	861 834	761	684	3422 $\nu(H_2O)$ 1622 $\delta(HOH)$
Erbium carbonate	1512	1455 1426	1092 1062	861 835	762	686	3406 $\nu(H_2O)$ 1622 $\delta(HOH)$

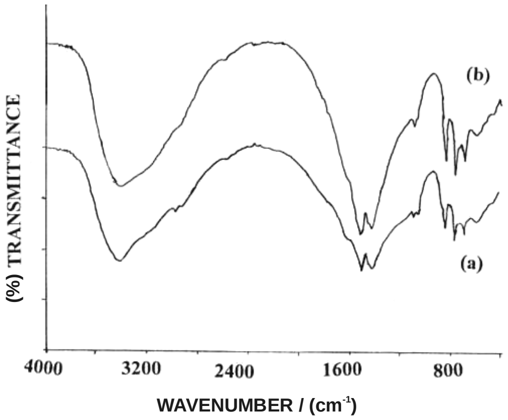
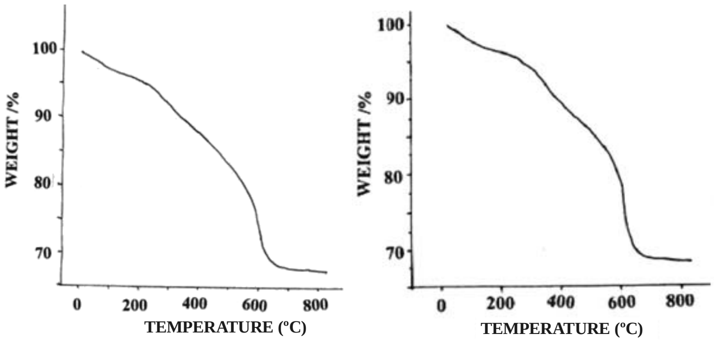


Fig. 3. IR spectra of holmium carbonate (a) and erbium carbonate (b)

The thermogravimetric curves (TG) for the holmium and erbium carbonate are shown in Fig. 4. The thermal decomposition of holmium and erbium carbonate contains dehydration and decarbonation processes. There is no evidence for the formation of any stable intermediate carbonate and the end product is Re_2O_3.



(a) (b)

Fig. 4. TG curves of holmium carbonate (a) and erbium carbonate (b)

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