A Synthetic Study of the Solid Solutions in the Systems $La_2(CO_3)_3 \cdot 8H_2O$-$Ce_2(CO_3)_3 \cdot 8H_2O$ and $La(OH)CO_3$-$Ce(OH)CO_3$

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The solid solutions in the systems $La_2(CO_3)_3 \cdot 8H_2O$–$Ce_2(CO_3)_3 \cdot 8H_2O$ and $La(OH)CO_3$–$Ce(OH)CO_3$ have been synthesized by the hydrolysis of the lanthanum–cerium trichloroacetates. The X-ray diffraction data of the solid solutions of $La_2(CO_3)_3 \cdot 8H_2O$–$Ce_2(CO_3)_3 \cdot 8H_2O$ indicated a lanthanite-type structure while the data of $La(OH)CO_3$–$Ce(OH)CO_3$ indicated a bastnaesite-type structure. The correlations between lanthanite, bastnaesite, and calkinsite, and the lanthanite-bastnaesite transformation are discussed.

Rare-earth carbonate minerals being mainly composed of lanthanum and cerium which have been reported are lanthanite, $(La,Ce)_2(CO_3)_3 \cdot 8H_2O$, calkinsite, $(La,Ce)_2(CO_3)_3 \cdot 4H_2O$, and bastnaesite, $(La,Ce)(F,OH)CO_3$.[1] Several double carbonate minerals, *e.g.*, ancylite, $(La,Ce)_x(Sr,Ca)_{2-x}(CO_3)_2(OH)_x \cdot (2-x)H_2O$, have also been described. However, because of the rare occurence and preparatory diffculties the existence and relationships between the minerals have not always been clear. The crystal structures of lanthanum carbonate octahydrate, $La_2(CO_3)_3 \cdot 8H_2O$,[2] and lanthanite, $(La,Ce)_2(CO_3)_3 \cdot 8H_2O$,[3] have been determined from X-ray diffraction studies. Despite differences in the representations of the unit cell parameters and space group, they were found to be isostructural. The principal structural features are infinite layers of RE–O(RE=La,Ce) coordination polyhedra and CO_3^{2-} groups. However the disordering of lanthanum and cerium has not been confirmed in the lanthanite-type carbonates. Furthermore, in spite of the existence with lanthanite, calkinsite which is considered to be the solid solution of lanthanum and cerium has not yet been the subject of chemical and mineralogical studies. It is not always apparent whether the structure of hydroxy-bastnaesite is isostructural with fluoro-bastnaesite or with ancylite ($x=2$).[4,5,13] Moreover, the existence of hydroxy-bastnaesite has not always been proposed.

In order to investigate the above mentioned points, solid solutions of the carbonates, changing the molar ratio of lanthanum to cerium have been synthesized at various temperatures and pressures, and the products examined by X-ray diffractometry, thermal analysis, and infrared spectroscopy.

Experimental

Synthesis of Rare-earth Carbonates. There are several precipitants for preparing rare-earth carbonates: alkali carbonates and bicarbonates, trichloroacetic acid, urea, *etc.*[6,14] Trichloroacetic acid was used as a precipitant in the present work, since it gives good crystalline products. An appropriate amount of 0.1 mol dm^{-3} lanthanum chloride solution and of 0.1 mol dm^{-3} cerium chloride solution were mixed together, maintaining a total volume of 10 cm^3. After the addition of a 5 cm^3 portion of 2.0 mol dm^{-3} trichloroacetic acid solution, the solution was adjusted with ammonia to pH 5—6 and the volume made up to 50 cm^3 with water. The solutions were placed in a thermostatted bath for a week at temperatures ranging from 50 to 80 °C and in glass autoclaves for four days at 100, 115, and 150 °C. The precipitates were filtered off, washed with water and air-dried.

X-Ray Powder Diffractometry. The X-ray powder diffractions were recorded on a Rigaku Denki Geigerflex Diffractometer, using Ni-filtered Cu $K\alpha$ radiation.

Chemical Analysis. The carbonates were analyzed by igniting weighed samples in a muffle furnace at a temperature of *ca.* 1000 °C. Loss on ignition corresponds to the CO_2+H_2O content of the sample. Both CO_2 and H_2O were determined by the routine procedure for elemental analysis for organic compounds. The ignited oxides were dissolved in perchloric acid. The determination of lanthanum and cerium in the dissolved solution was conducted according to the conventional method.

Infrared Spectra. The infrared absorption spectra of the carbonates were obtained by means of a JASCO IRA-1 spectrophotometer, using KBr pellets and the nujol mull techniques.

Thermal Analysis. The thermal decomposition processes of the carbonates were investigated with a Rigaku Denki Thermoflex thermalanalyzer. About twenty milligramme samples in shallow platinum crucibles were heated in air or in a stream of nitrogen at a heating rate of 5 °C/min.

Electron Probe Microanalysis. The compositional analyses of the carbonates were conducted by means of a JEOL JXA-5 scanning electron microscopic analyzer, using the characteristic X-rays of La $L\alpha$ and Ce $L\alpha$.

Results and Discussion

X-Ray Powder Diffractometry. The carbonates synthesized at 50 and 65 °C gave patterns similar to that of lanthanite, while the carbonates synthesized at 100 °C (5.5 atm) and 115 °C (8 atm) gave patterns similar to that of bastnaesite. The carbonates synthesized from lanthanum-rich solutions at 80 °C gave patterns consisting of those of lanthanite and bastnaesite. The molar ratio of lanthanum to cerium in the lanthanum-rich solutions was 6 or more. No precipitates appeared when the mixed solutions were kept at 150 °C. The X-ray data of the carbonates synthesized at 100 °C (5.5 atm) are shown in Table 1. An observed increase in d values with increasing molar ratio of lanthanum indicates that the carbonates formed solid solutions. Furthermore, when samples of the synthesized carbonates were physically mixed with the two end-members (*i.e.* bastnaesite lanthnum and cerium carbonate) the position and intensity of the diffraction peaks from the synthesized material could be described as just the average and sum, respectively, of the two end-members. The electron probe microanalysis also

Table 1. X-Ray powder data for bastnaesite-type carbonates

hkl	*d*(Å)							I/I_0
	La10	La8Ce2	La6Ce4	La5Ce5	La4Ce6	La2Ce8	Ce10	
002	5.031	5.022	5.002	5.000	4.994	4.991	4.988	70
300	3.661	3.655	3.642	3.639	3.635	3.627	3.622	90
302	2.955	2.952	2.942	2.939	2.936	2.932	2.927	100
004	2.504	2.505	2.497	2.497	2.494	2.491	2.489	15
330	2.112	2.107	2.100	2.098	2.096	2.092	2.090	30
304	2.066	2.064	2.058	2.057	2.055	2.052	2.051	45
332	1.944	1.942	1.936	1.934	1.933	1.929	1.926	25
600	1.827	1.825	1.818	1.817	1.815	1.812	1.810	10
602	1.716	1.714	1.709	1.707	1.706	1.702	1.700	15
334	1.612	1.611	1.607	1.605	1.604	1.602	1.601	10
a(Å)	12.68	12.66	12.62	12.61	12.59	12.56	12.55	
c(Å)	10.06	10.04	10.01	10.00	9.988	9.982	9.976	

The abbreviations used in this table are the figures of molar ratios of lanthanum and cerium in the starting solutions (1 Å=0.1 nm).

Table 2. Chemical analysis of synthesized carbonates

Lanthanite-type			Bastnaesite-type		
La : Ce Mixed	La : Ce Found	M_2O_3 : CO_2 : H_2O	La : Ce Mixed	La : Ce Found	M_2O_3 : CO_2 : H_2O
10 : 0	10 : 0	1.00 : 3.09 : 7.40	10 : 0	10 : 0	1.00 : 2.19 : 1.84
8 : 2	7.88 : 2.12	1.00 : 3.14 : 7.74	8 : 2	8.02 : 1.98	1.00 : 2.12 : 2.13
6 : 4	6.00 : 4.00	1.00 : 3.18 : 7.64	6 : 4	5.92 : 4.08	1.00 : 2.03 : 2.39
5 : 5	5.00 : 5.00	1.00 : 3.09 : 7.91	5 : 5	5.02 : 4.98	1.00 : 2.08 : 1.87
4 : 6	3.95 : 6.05	1.00 : 3.10 : 7.78	4 : 6	3.98 : 6.02	1.00 : 2.05 : 2.15
2 : 8	1.96 : 8.04	1.00 : 3.06 : 7.79	2 : 8	2.00 : 8.00	1.00 : 2.15 : 2.20
0 : 10	0 : 10	1.00 : 2.98 : 7.68	0 : 10	0 : 10	1.00 : 2.11 : 2.27

M_2O_3 is the sum of lanthanum and cerium oxides.

indicated that the bastnaesite-type carbonates formed solid solutions over the whole series. Assuming a hexagonal symmetry,[12] the unit cell parameters, *a* and *c*, were calculated from 300 and 002 diffractions respectively (Table 1). These cell parameters indicated, semiquantitatively, the molar ratios of lanthanum and cerium in bastnaesite-type carbonates. The shift of the diffraction peaks of the lanthanite-type carbonates were too small to analyze, however, the results of the electron probe microanalysis indicated that lanthanite-type carbonates formed solid solutions.

Chemical Analysis. From the results shown in Table 2, the molar ratios of lanthanum to cerium contained in the synthesized carbonates were almost equal to those in the starting solutions. In addition, it was found that the molar ratio M_2O_3: CO_2: H_2O was almost 1: 3: 8 for the carbonates synthesized at 50 °C under atmospheric pressure and 1: 2: 2 for those synthesized at 100 °C, 5.5 atm. The chemical composition of the carbonates synthesized at 50 °C agreed with the composition of lanthanite, while the composition of those synthesized at 100 °C, 5.5 atm agreed with the composition of hydroxy-bastnaesite, assuming one water molecule of adhesive moisture. From the results of X-ray diffractometry and chemical analysis, it became apparent that $La_2(CO_3)_3 \cdot 8H_2O$ and $Ce_2(CO_3)_3 \cdot 8H_2O$ form a complete series of lanthanite-type solid solutions by the isomorphous replacement of lanthanum by cerium, and that $La(OH)CO_3$ and $Ce(OH)CO_3$ form a complete series of bastnaesite-type solid solutions by the isomorphous replacement of lanthanum by cerium.

Infrared Spectroscopy. The infrared spectra of the lanthanite-type and bastnaesite-type carbonates are shown in Fig. 1. The frequencies for the four modes of the free carbonate ion are: ν_1, 1063 cm^{-1}; ν_2, 879 cm^{-1}; ν_3, 1415 cm^{-1}; and ν_4, 680 cm^{-1}. The vibrations ν_3 and ν_4 are degenerate while ν_1 is infrared-inactive for

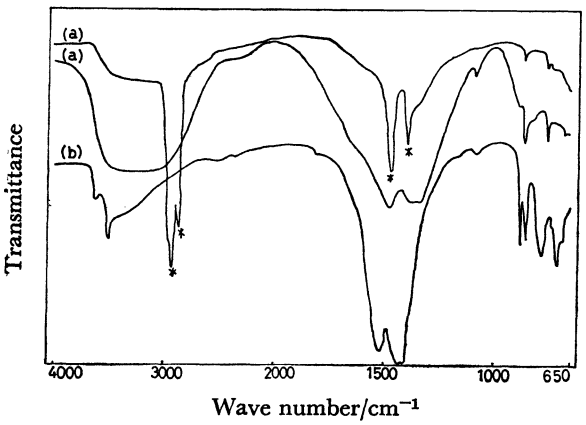


Fig. 1. Infrared absorption spectra of synthesized carbonates.
(a) Lanthanite-type (in KBr disk and in Nujol mull),
(b) bastnaesite-type (in KBr disk).

the free ion.[8] For the lanthanite-type carbonate, the ν_1 mode was just detectable while the ν_3 mode split, indicating that the D_{3h} symmetry of the free carbonate ion was lowered either to C_{2v} or to C_s. The bands in the region 2900—3500 cm^{-1}, appeared even in nujol mull, and were assigned to the absorption of water. Bands marked by a star (*) in Fig. 1 are the absorptions attributable to Nujol. For the bastnaesite-type carbonate, the ν_1 mode appeared faintly and the degenerate mode, ν_3, split. The splitting of the non-degenerate mode, ν_2, indicated that non-equivalent carbonate groups existed.[9] The sharp absorption bands at 3630 and 3480 cm^{-1} were attributed to absorptions by the OH group.[5] The shifts and changes of the absorption spectra caused by the formation of solid solutions were not observed over all the absorptions.

Thermal Analysis. The thermal analysis of the carbonates having various molar ratios of lanthanum and cerium are shown in Fig. 2-a. On the thermogravimetric curve (TG) for the lanthanite-type La10 carbonate, the following abbreviations are used: La10, $La_2(CO_3)_3 \cdot 8H_2O$; Ce10, $Ce_2(CO_3)_3 \cdot 8H_2O$; La5Ce5, $(La_{1.00}Ce_{1.00})_2(CO_3)_3 \cdot 8H_2O$. Initially there was loss of water, which corresponded to the formation of the anhydrous carbonate. Continuous raising of the temperature led to the formation of the dioxide carbonate. The final product of the decomposition was La_2O_3. From the differential scanning calorimetric curve (DSC) for the La10 carbonate, it has been established that the dehydration and decarbonatation in this decomposition process were endothermic. As for the lanthanite-type Ce10 carbonate, the loss of the CO_2 molecules after dehydration was accompanied by the oxidation of Ce^{3+}. That no peaks appeared in the DSC at *ca.* 250 °C appear to be the net result of an endothermic decomposition due to decarbonation coupled with an exothermic reaction due to the oxidation of Ce^{3+} to Ce^{4+}. Although the continuous raising of the temperature in air did not lead to the formation of the dioxide carbonate, it did lead to the formation of the dioxide carbonate, $Ce_2O_2CO_3$ at *ca.* 400 °C in a stream of nitrogen (Fig. 2-c). However, the dioxide carbonate decomposed immediately to CeO_2. The lanthanite-type La5Ce5 carbonate lost eight water molecules at one time under the heating rate used here (5 °C/min), while the formation of the dioxide carbonate did not appear in air. It did, however, appear in a stream of nitrogen. No clear peak attributable to decarbonatation appeared in the DSC at *ca.* 450 °C. As in the course of the decomposition of the Ce10 carbonate, this is the net result of endothermic and the exothermic reactions. The results of the thermal analysis of the lanthanite-type carbonates of other molar ratios were similar to that of the La5Ce5 carbonate. The end product of the La5Ce5 carbonate was a mixed La(III)--Ce(IV)-oxide. The intermediate $Ln_2O_3 \cdot xCO_2 (x<1)$ reported by other workers was not observed.[9]

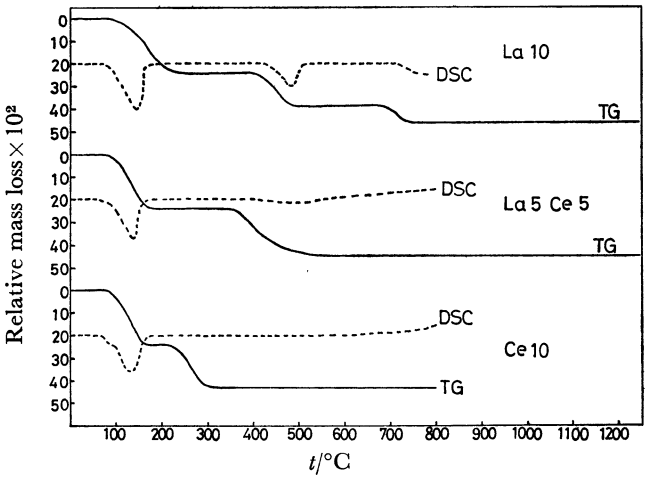


Fig. 2a. TG and DSC curves of lanthanite-type carbonates (in air).

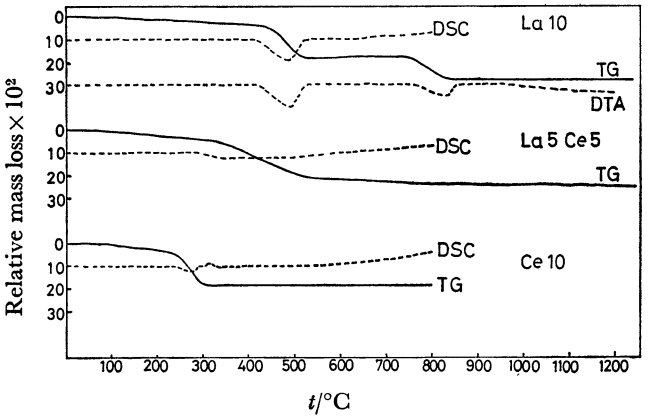


Fig. 2b. TG and DSC curves of bastnaesite-type carbonates (in air).

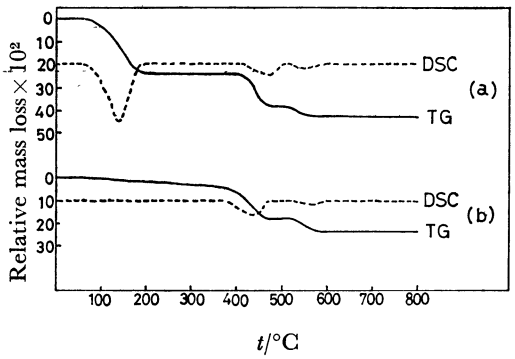


Fig. 2c. TG and DSC curves of lanthanite-type and bastnaesite-type carbonates (in nitrogen stream).
(a) $Ce_2(CO_3)_3 \cdot 8H_2O$, (b) $Ce(OH)CO_3 \cdot H_2O$.

In air:

$$La_2(CO_3)_3 \cdot 8H_2O \xrightarrow{ca.\ 80\ ^\circ C} La_2(CO_3)_3 \xrightarrow{ca.\ 400\ ^\circ C} La_2O_2CO_3\text{(IA type)} \xrightarrow{ca.\ 680\ ^\circ C} La_2O_3$$

$$(La_{1.00}Ce_{1.00})_2(CO_3)_3 \cdot 8H_2O \xrightarrow{ca.\ 80\ ^\circ C} (La_{1.00}Ce_{1.00})_2(CO_3)_3 \xrightarrow{ca.\ 330\ ^\circ C} La_2O_3 + CeO_2$$

$$Ce_2(CO_3)_3 \cdot 8H_2O \xrightarrow{ca.\ 70\ ^\circ C} Ce_2(CO_3)_3 \xrightarrow{ca.\ 210\ ^\circ C} CeO$$

In a stream of nitrogen:

$$Ce_2(CO_3)_3\cdot 8H_2O \xrightarrow{ca.\ 60\ ^\circ C} Ce_2(CO_3)_3 \xrightarrow{ca.\ 400^\circ C} Ce_2O_2CO_3 \xrightarrow{ca.\ 500\ ^\circ C} CeO_2$$

$$(La_{1.00}Ce_{1.00})_2(CO_3)_3\cdot 8H_2O \xrightarrow{ca.\ 70\ ^\circ C} (La_{1.00}Ce_{1.00})_2(CO_3)_3 \xrightarrow{ca.\ 430\ ^\circ C} (La_{1.00}Ce_{1.00})_2O_2(CO_3) \xrightarrow{ca.\ 540\ ^\circ C} La_2O_3 + CeO_2$$

Figure 2-b shows the decomposition of bastnaesite-type carbonates. For the bastnaesite-type La10 carbonate, the following abbreviations are used here: La10, $La(OH)CO_3\cdot H_2O$; Ce10, $Ce(OH)CO_3\cdot H_2O$; La5Ce5, $(La_{0.50}Ce_{0.50})(OH)CO_3\cdot H_2O$. The bastnaesite-type La10 carbonate started losing adhesive moisture *ca.* 100 °C and the main decomposition occurred at *ca.* 430 °C accompanying the formation of the dioxide carbonate. The evolution of the remaining one mole of CO_2 began at *ca.* 740 °C. The decomposition of the Ce10 carbonate was accompanied by the oxidation of Ce^{3+}. The small peak that appeared in the DSC at *ca.* 300 °C appeared to be the net result of an endothermic decomposition reaction due to the dehydration and decarbonatation and an exothermic reaction due to the oxidation of Ce^{3+} to Ce^{4+}. The La5Ce5 carbonate continuously lost weight from *ca.* 70 °C. The dioxide carbonate decomposed from the lanthanite-type and bastnaesite-type samples showed different infrared and X-ray powder diffraction spectra. According to the literature, the former was found to be IA type (monoclinic) and the latter, to be II type (hexagonal).[9]

In air:

$$La(OH)CO_3\cdot H_2O \xrightarrow{ca.\ 100\ ^\circ C} La(OH)CO_3 \xrightarrow{ca.\ 430\ ^\circ C} La_2O_2CO_3(\text{II type}) \xrightarrow{ca.\ 740\ ^\circ C} La_2O_3$$

$$(La_{1.00}Ce_{1.00})(OH)CO_3\cdot H_2O \xrightarrow{ca.\ 70\ ^\circ C} (La_{1.00}Ce_{1.00})(OH)CO_3 \xrightarrow{ca.\ 290\ ^\circ C} La_2O_3 + CeO_2$$

$$Ce(OH)CO_3\cdot H_2O \xrightarrow{ca.\ 70\ ^\circ C} Ce(OH)CO_3 \xrightarrow{ca.\ 230\ ^\circ C} CeO_2$$

In a stream of nitrogen:

$$Ce(OH)CO_3\cdot H_2O \xrightarrow{ca.\ 70\ ^\circ C} Ce(OH)CO_3 \xrightarrow{ca.\ 370\ ^\circ C} Ce_2O_2CO_3 \xrightarrow{ca.\ 510\ ^\circ C} CeO_2$$

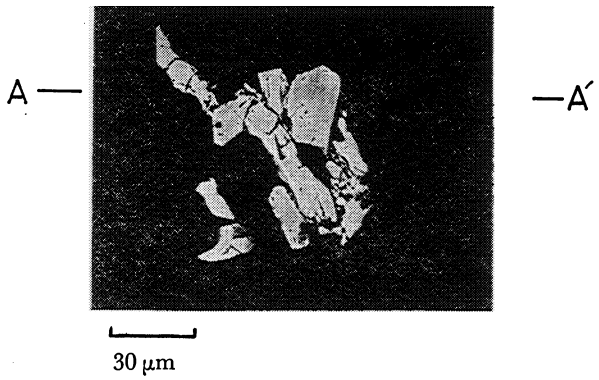
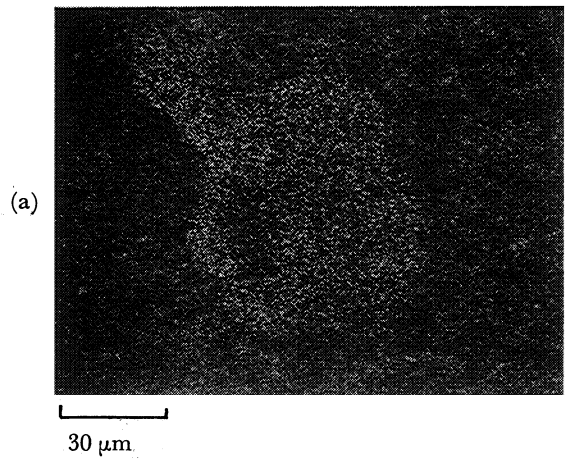


Fig. 3a. The compositional figure of the bastnaesite-type La4Ce6 carbonate.

$$(La_{1.00}Ce_{1.00})(OH)CO_3\cdot H_2O \xrightarrow{ca.\ 100\ ^\circ C} (La_{1.00}Ce_{1.00})(OH)CO_3 \xrightarrow{ca.\ 390\ ^\circ C} (La_{1.00}Ce_{1.00})_2O_2CO_3 \xrightarrow{ca.\ 550\ ^\circ C} La_2O_3 + CeO_2$$



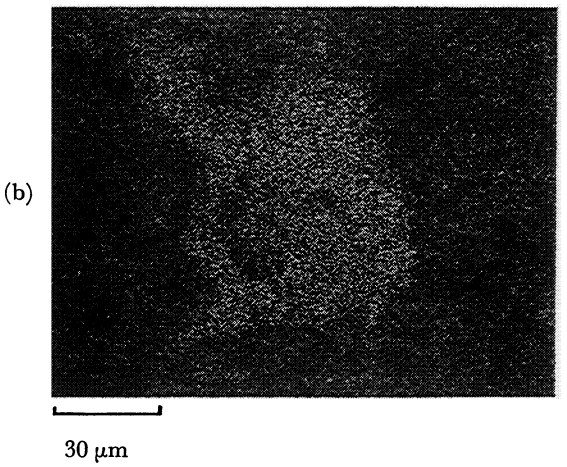


Fig. 3b. The characteristic X-ray figures of the bastnaesitetype La4Ce6 carbonate.
(a) La Lα, (b) Ce Lα.

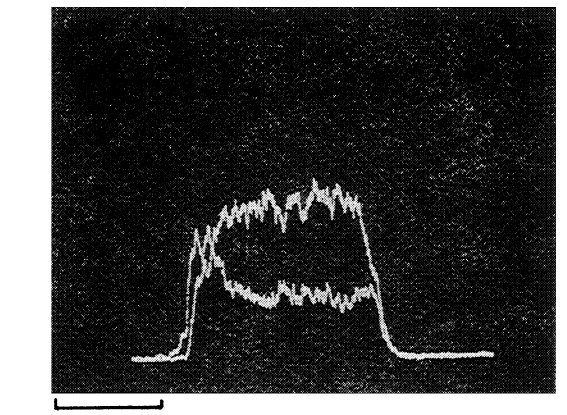


Fig. 3c. The line profiles of the bastnaesite-type La4Ce6 carbonate in A-A′ section.
Upper line: Ce *Lα*, lower line: La *Lα*.

Calkinite[10] was discovered as a late mineral associated with lanthanite in the veins in Bearpaw Mountains of Montana. Although its occurrence is very similar to that of lanthanite and the other hydrated rare earth orthocarbonate minerals synthesized, calkinsite has not been obtained as a product of the La5Ce5 carbonate or as an intermediate of the thermal decomposition of any of the synthesized rare-earth carbonates.

Lanthanite is usually rarely found associating with bastnaesite. The reason for its rare occurrence becomes clear from the above discussions and experiments. Lanthanite changed its structure and chemical composition from lanthanite- to bastnaesite-type when heated with water at 100 °C.[11,12] Thus, it is presumed that lanthanite is lacking in nature due to this thermal metamorphism.

Electron Probe Microanalysis. The compositional figure of the bastnaesite-type La4Ce6 carbonate and its characteristic X-ray figures of La $L\alpha$ and Ce $L\alpha$ are shown in Fig. 3. From the characteristic X-ray figures of La $L\alpha$ and Ce $L\alpha$ and the line profiles in a grain of the La5Ce5 carbonates, the same grain was found to contain equal molar ratios of lanthanum and cerium, indicating that the carbonate formed a solid solution. Semiquantitative analysis suggested that there was a slight difference in the composition of each grain, which might be a reflection of some "fluctuation" in this solution. The molar ratio of lanthanum to cerium contained in the crystal was also microscopically equal to that of the starting solution.

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