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Hans-Juergen Meyer. An Improved Synthesis of Ternary Carbonates: The Examples $\text{LiLa}(\text{CO}_3)_2$ and $\text{La}(\text{CO}_3)\text{F}$. *Journal of Inorganic and General Chemistry / Zeitschrift für anorganische und allgemeine Chemie*, 2010, 636 (15), pp.2622. 10.1002/zaac.201000198 . hal-00574813

HAL Id: hal-00574813

<https://hal.science/hal-00574813>

Submitted on 9 Mar 2011

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**An Improved Synthesis of Ternary Carbonates: The
Examples $\text{LiLa}(\text{CO}_3)_2$ and $\text{La}(\text{CO}_3)\text{F}$**

Journal:	<i>Zeitschrift für Anorganische und Allgemeine Chemie</i>
Manuscript ID:	zaac.201000198.R1
Wiley - Manuscript type:	Article
Date Submitted by the Author:	15-Jun-2010
Complete List of Authors:	Meyer, Hans-Juergen
Keywords:	Rare Earth, Carbonate



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3 **An Improved Synthesis of Ternary Carbonates: The Examples $\text{LiLa}(\text{CO}_3)_2$ and**
4 **$\text{La}(\text{CO}_3)\text{F}$**
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8 **Jochen Glaser,^[a] and H.-Jürgen Meyer^{*[a]}**
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11 **Keywords:** Rare earth; Carbonate; Metathesis, Crystal Structure; Luminescence
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15 **Abstract.** The ternary carbonate $\text{LiLa}(\text{CO}_3)_2$, previously obtained under supercritical CO_2
16 pressure conditions was prepared by a new and efficient way of synthesis. A 2:1 molar mixture
17 of $\text{Li}_2(\text{CO}_3)$ and LaCl_3 was reacted in a silica tube at 400 °C. The crystal structure of $\text{LiLa}(\text{CO}_3)_2$
18 was refined from X-ray single-crystal data and can be related with a caesium chloride type
19 arrangement where Li^+ and La^{3+} ions occupy the caesium positions and $(\text{CO}_3)^{2-}$ ions occupy all
20 cubic voids. Cerium-doped samples ($\text{LiLa}(\text{CO}_3)_2:\text{Ce}$) exhibit blue luminescence. The mineral
21 bastnäsite was synthesized by the same preparative approach, departing from a 1:1 molar
22 mixture of LaF_3 and $\text{Li}_2(\text{CO}_3)$ being reacted at 450 °C.
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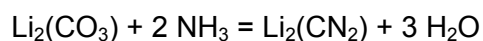
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Introduction

Carbonates of the rare earth (RE) elements with the expected formula $RE_2(CO_3)_3$ remain a missing group of compounds, although the chemistry of corresponding carbodiimides has been recently developed, i.e. for the formula type $RE_2(CN_2)_3$ with $RE = Y, Ce - Lu$ [1]. The chemical relationship between carbodiimides and carbonates may be reflected by the synthesis of carbodiimide through ammonolysis reaction of a metal carbonate, and oppositely, by the decomposition of carbodiimide into carbonate in the presence of moist air or water, with a typical example being represented by the corresponding lithium compounds [2]:



Rare earth carbonates are known as hydrates, like $La_2(CO_3)_3 \cdot (H_2O)_8$ [3] being crystallized from aqueous solutions of $La(NO_3)_3 \cdot 6H_2O$ and $NaHCO_3$. The thermal decomposition of $La_2(CO_3)_3 \cdot 8H_2O$ takes course over several steps. Unfortunately, the dioxide monocarbonate $La_2O_2(CO_3) \cdot 3H_2O^4$ is already formed below 150 °C to yield $La_2O_2(CO_3)$ [5] near 400 °C [6]. Ammonolysis reactions of lanthanum carbonate hydrate have shown to yield lanthanum dioxide monocarbodiimide $La_2O_2(CN_2)$ [7]. Therefore this preparative way has been considered inapplicable for the synthesis of anoxic carbodiimide compounds. [8]

Ternary carbonate hydrate compounds having the general formula $ARE(CO_3)_2 \cdot xH_2O$ ($A =$ alkaline metal; $RE =$ rare earth metal) have been already reported one-hundred years ago when their different solubilities were studied in attempt to develop a separation process for lanthanide elements. [9] A dehydration process of these compounds for the observation of non-aqueous compounds appears generally difficult, due to formation of dioxide monocarbonates ($RE_2O_2(CO_3)$).

A synthesis route for anhydrous ternary carbonates developed by Seidel and coworkers, departing from autoclave reactions of mixtures of alkali carbonates and rare earth oxalates, A_2CO_3 and $RE_2(C_2O_4)_3 \cdot xH_2O$, under 2000 bar CO_2 pressure at 500 °C. Reactions with $A = Li$ have yielded two monoclinic modifications of compounds having the general formula $LiRE(CO_3)_2$ ($RE = Y, La - Lu$), but the crystal structures of these compounds are unknown. [10] Syntheses of $ARE(CO_3)_2$ compounds with $A = Na, K$ and $RE = Y, La - Lu$ were also reported following this way of synthesis. [11] The effort in operating equipment and performance related with the high-pressure synthesis of anhydrous carbonate compounds is due the relatively low thermal decomposition temperatures, in case of $LiLa(CO_3)_2$ being obtained slightly above 400 °C. In this contribution a new and simple way of synthesis is described for the observation single crystalline

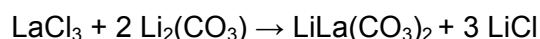
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3 LiLa(CO₃)₂. In addition, the crystal structure and luminescence behaviour of a Cerium-doped
4 sample of LiLa(CO₃)₂ are reported
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8 **Experimental Section**

9 **Syntheses**

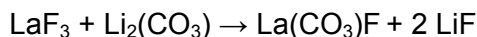
10 The synthesis of LiLa(CO₃)₂ was successfully performed by solid state metathesis reaction from
11 LaCl₃ and Li₂(CO₃) following a corresponding approach used for the synthesis of LiLa(CN₂)₂ [12]
12 departing from LaCl₃ and Li₂(CN₂). A 1:2 molar ratio of starting materials, LaCl₃ (ABCR, 99.9 %)
13 and Li₂(CO₃) (Alfa, ultrapure) was carefully ground in an agate mortar and loaded into a dry silica
14 tube under inert gas conditions (glove box). The absence of contaminations with oxygen or
15 water was crucial for the success of the reaction.
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18 The argon filled silica tubes containing the reaction mixtures (total mass ca. 200 mg) were flame
19 sealed under vacuum, transferred into a tube furnace and heated at 400 °C for 12 - 24 hours.
20 After cooling to room temperature by the natural cooling rate of the furnace, crystalline mixtures
21 of LiLa(CO₃)₂ and LiCl were obtained as reaction products by X-ray powder diffraction, without a
22 detectable side-phase. Thus, the reaction may be described following the equation:
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26 Doped samples of LiLa(CO₃)₂:Ce were synthesised by substituting 5 mol% of LaCl₃ by CeCl₃
27 and reacted under identical conditions as described before. Single-crystals of LiLa(CO₃)₂ were
28 obtained when reacting the same LaCl₃/Li₂(CO₃) mixture with (≈ 2/3 equivalents) KCl in order to
29 achieve an eutectic LiCl/KCl flux [13]. Products were washed with water to remove LiCl and the
30 salt flux, respectively.
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33 The same type of reactions was successfully performed for the synthesis of La(CO₃)F
34 (Bastnäsit). A corresponding 1:1 molar mixture of LaF₃ and Li₂(CO₃) was reacted in a silica tube
35 to yield La(CO₃)F at 450 °C, according to the equation:
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39 **X-Ray Powder Diffraction**

40 Diffraction data were collected on a Stoe StadiP X-ray powder diffractometer using Ge-
41 monochromatized Cu-K_{α1} radiation. The powder pattern of LiLa(CO₃)₂ was indexed
42 monoclinically (from 27 reflections) yielding lattice parameters of $a = 6.901(2)$ Å, $b = 7.842(2)$ Å,
43 $c = 8.432(2)$ Å, and $\beta = 97.25(2)^\circ$. The powder pattern of La(CO₃)F (Bastnäsit) was indexed
44 hexagonally (from 10 reflections) to yield $a = 7.173(4)$ Å, and $c = 9.823(6)$ Å.
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X-Ray Single-Crystal Diffraction

Transparent single-crystals of $\text{LiLa}(\text{CO}_3)_2$ were selected and fixed on the tip of glass fibers for a single-crystal diffraction measurement (Stoe IPDS diffractometer, graphite monochromatized Mo-K_α radiation) at room temperature (Table 1). Intensities were corrected for Lorentz factors, polarisation and absorption effects. $\text{LiLa}(\text{CO}_3)_2$ was found to crystallize in the monoclinic space group $I2/a$. The structure refinement including anisotropic refinements of all atoms with the program SHELX [14] resulted in $R1 = 0.0146$, $wR2 = 0.0366$ for all measured X-ray intensities. Crystallographic data are given in Table 2 and selected interatomic distances are provided in Table 3.

Photoluminescence Studies

A fluorescence spectrometer (Edinburgh Instrument, FS920, equipped with a 450 W Xe-lamp) was used for the measurement of excitation and emission spectra, all monitored by a cooled photomultiplier tube (Hamamatsu R2658, detection range: 300 – 1010 nm) driven in a single photon counting mode.

Results and Discussion

The development of preparative routes for the synthesis of thermally moderately stable compounds is a great temptation in preparative chemistry because thermally labile solid state compounds may be regarded as the largest missing group compounds, with potential to exhibit new or enhanced functionalities. Several examples of solid state metathesis (SSM) reactions have been already successfully performed in a temperature region between 400 – 600 °C. [15]

A variety of rare earth carbodiimide compounds, i.e. those with the formula type $\text{RE}_2(\text{CN}_2)_3$ were accomplished by SSM reactions departing from mixtures containing $\text{Li}_2(\text{CN}_2)$ and RECl_3 . Exothermic reactions are obtained above 400 °C, sometimes near 500 °C, depending on the individual RECl_3 compound used, as can be monitored by thermo-analytic studies. The employment of a eutectic LiCl/KCl flux (melting point: ≈ 354 °C) has been advantageous in these reactions especially for single-crystal growth. Still lower reaction temperatures may be achieved by using an appropriate melt, or even a catalyst.

Binary rare earth carbonates that may be assigned with the expected formula $\text{RE}_2(\text{CO}_3)_2$ remain unknown to date, whereas their carbodiimide counterparts have been developed, e.g. for the already mentioned formula type $\text{RE}_2(\text{CN}_2)_3$. Thermal stabilities of most rare earth carbodiimide

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3 compounds range up to 650 – 750 °C and restrict any preparative attempt to operate below the
4 decomposition temperature. The carbodiimide ion, which may be also assigned as
5 dinitridocarbonate, is related with the (oxo-)carbonate ion by the same charge, by similar limited
6 thermal stability, and by chemical transformation into each other mentioned in the introduction.
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10 Thermal decomposition studies of $\text{LiLa}(\text{CO}_3)_2$ have already shown a decomposition to occur
11 slightly above 400 °C. Therefore, all preparative attempts were restricted to this maximum
12 temperature. The straight forward synthesis of a 2:3 molar mixture was successful for the
13 preparation of pure $\text{LiLa}(\text{CO}_3)_2$. No excess pressure was noticeable when opening the silica
14 vessel containing the reaction product. A reaction performed with a 2:3 molar mixture of LaCl_3
15 and $\text{Li}_2(\text{CO}_3)$ targeting the composition $\text{La}_2(\text{CO}_3)_3$ yielded $\text{LiLa}(\text{CO}_3)_2$ plus side phases.
16 Corresponding experiments departing from LaF_3 and $\text{Li}_2(\text{CO}_3)$ yielded $\text{La}(\text{CO}_3)\text{F}$.
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19 The counterpart of $\text{LiLa}(\text{CO}_3)_2$ in carbodiimide chemistry is $\text{LiLa}(\text{CN}_2)_2$. The unknown crystal
20 structure of $\text{LiLa}(\text{CO}_3)_2$ was refined on a single-crystal. The assignment of a monoclinic crystal
21 system and the unit cell dimensions (Table 1) were consistent with the previously reported
22 results.¹⁰ The crystal structure of $\text{LiLa}(\text{CO}_3)_2$, refined in this work for the first time can be
23 considered to follow motif of the caesium chloride structure, in which Li^+ and La^{3+} ions are
24 arranged to occupy positions of Cs^+ ions and carbonate groups occupy all cubic voids of this
25 arrangement (Figure 1). In fact, this idealized arrangement is clearly distorted as a result of the
26 planarity and orientation of the carbonate group to allow for different nearest neighbour
27 interactions with cations. Lithium ions are surrounded by four carbonate groups forming a
28 distorted $[\text{LiO}_4]$ tetrahedron with oxygen atoms of four carbonate groups (Figure 2). Lanthanum
29 ions are surrounded by eight carbonate groups forming a distorted square antiprismatic
30 arrangement with their carbon atoms (Figure 2). The arrangement of carbonate groups results in
31 two bidentate nearest neighbor interactions and six monodentate interactions via oxygen atoms,
32 resulting in the coordination number of ten at the lanthanum atom. The carbonate ion in the
33 structure itself appears almost planar (Table 3).
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45 The potential of $\text{LiLa}(\text{CO}_3)_2$ as a luminescent material was investigated by luminescence
46 measurement on Ce^{3+} doped samples of $\text{LiLa}_{1-x}\text{Ce}_x(\text{CO}_3)_2$ with $x = 0.05$. The luminescence
47 spectra of the Ce^{3+} doped materials are governed by an interconfigurational transition between
48 the ground state levels ($^2\text{F}_{5/2}$ and $^2\text{F}_{7/2}$) of the $[\text{Xe}]4\text{f}^1$ configuration and the lowest crystal-field
49 components of the $[\text{Xe}]5\text{d}^1$ configuration. This is a spin and parity allowed transition, resulting in
50 high oscillator strength and a short decay constant. Due to the involvement of d-orbitals into
51 chemical bonding, the energy of the crystal-field components of the $[\text{Xe}]5\text{d}^1$ configuration is a
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3 sensitive function of the chemical environment. Ce^{3+} activated luminescent materials can thus
4 show UV, blue, green, or red luminescence, whereby the energetic position of the absorption
5 and emission bands are determined by the crystal-field strength and the covalent character of
6 the lattice position, where Ce^{3+} is localized. In case of $\text{LiLa}(\text{CO}_3)_2:\text{Ce}$ a blue emission is observed
7 near 410 nm and the excitation spectrum monitored for the emission at 400 nm reveals two
8 bands located at 315 and 285 nm (Figure 3).
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13 **Acknowledgment**

14
15 We are indebted to Dr. Helga Bettentrup and Prof. Dr. Thomas Jüstel from the University of
16 Applied Sciences (FH Münster) in Steinfurt for recording luminescence data on $\text{LiLa}(\text{CO}_3)_2:\text{Ce}$.
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Table 1. Crystal data and structure refinement for LiLa(CO₃)₂.

Empirical formula	LiLaC ₂ O ₆
Formula weight	265.87
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	<i>I</i> 2/a
Unit cell dimensions	<i>a</i> = 6.888(2) Å
	<i>b</i> = 7.853(1) Å
	<i>c</i> = 8.429(2) Å
	β = 97.24(3)°
Volume	452.3(2) Å ³
Z	4
Density (calculated)	3.905 g/cm ³
Absorption coefficient	9.393 mm ⁻¹
F(000)	480
Crystal size	0.2 0 x 0.06 x 0.06 mm ⁻¹
Θ -range for data collection	3.95 to 25.91°.
Index ranges	-8 ≤ <i>h</i> ≤ 8; -9 ≤ <i>k</i> ≤ 9; -10 ≤ <i>l</i> ≤ 10
Reflections collected	2400
Independent reflections	441 [R(int) = 0.0353]
Completeness in 2 Θ = 25.91°	99.3 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	441 / 0 / 47
Goodness-of-fit on F ²	1.178
Final R indices [<i>I</i> > 2 σ (<i>I</i>)]	R1 = 0.0144, wR2 = 0.0365
R indices (all data)	R1 = 0.0146, wR2 = 0.0366
Largest diff. peak and hole	0.705 and -0.770 e·Å ³

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \cdot 10^3$) for $\text{LiLa}(\text{CO}_3)_2$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Li(1)	3/4	0.2515(11)	0	14(1)
La(1)	1/4	0.1946(1)	0	8(1)
O(1)	-0.0634(3)	0.3303(3)	-0.1241(3)	13(1)
O(2)	0.4261(3)	-0.0851(3)	0.1207(2)	12(1)
O(3)	0.1821(3)	0.4152(3)	0.2025(2)	14(1)
C(1)	0.3963(4)	-0.0581(3)	0.2678(3)	10(1)

Table 3. Selected Interatomic Distances (in \AA) and O-C-O Angles (in $^\circ$) for $\text{LiLa}(\text{CO}_3)_2$.

Li(1)-O(1)	1.862(4)	x2
Li(1)-O(2)	1.975(6)	x2
La(1)-O(1)	2.514(2)	x2
La(1)-O(3)	2.517(2)	x2
La(1)-O(3)	2.637(2)	x2
La(1)-O(2)	2.649(2)	x2
La(1)-O(2)	2.706(2)	x2
C(1)-O(1)	1.270(4)	
C(1)-O(2)	1.300(3)	
C(1)-O(3)	1.283(3)	
O(1)-C(1)-O(3)	121.5(3)	
O(1)-C(1)-O(2)	121.7(2)	
O(3)-C(1)-O(2)	116.7(2)	

Figure Captions:

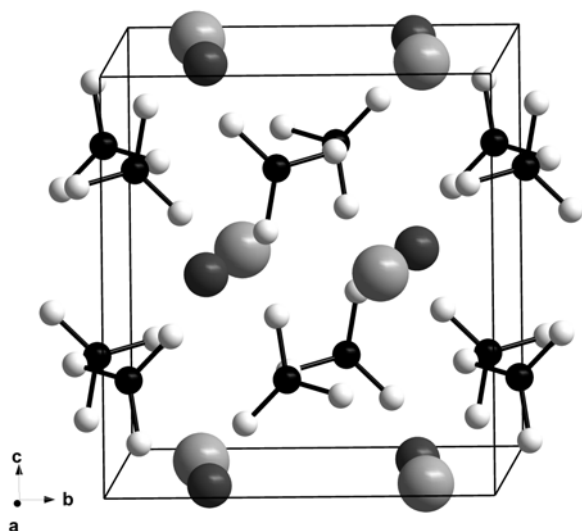


Figure 1. Projection of a section of the $\text{LiLa}(\text{CO}_3)_2$ structure with the unit cell shown (Li ions are shown dark grey and La light grey).

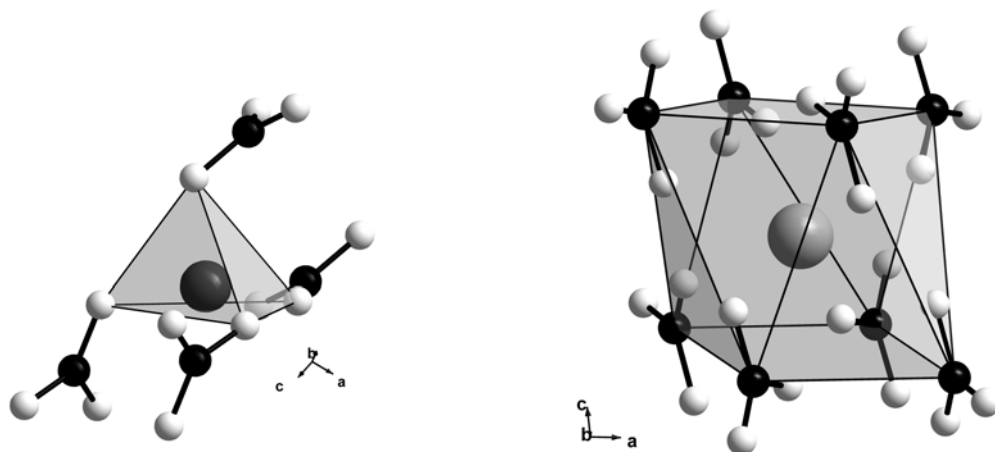


Figure 2. Arrangement of carbonate groups around lithium (left) and lanthanum (right) ions.

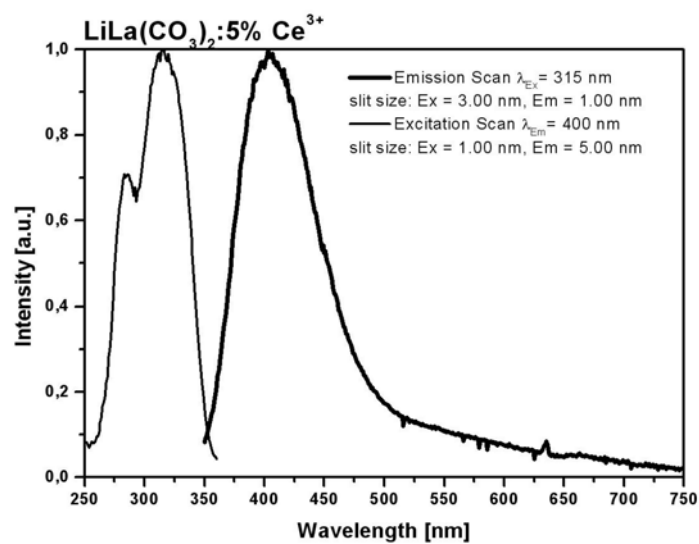


Figure 3. Excitation and emission spectrum of $\text{LiLa}(\text{CO}_3)_2:\text{Ce}$.

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