

Crystal Growth and Characterization of the Rare Earth Fluoride Carbonates
 $\text{NaLnCO}_3\text{F}_2$ ($\text{Ln} = \text{Eu-Lu}$)

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Abstract

A series of rare-earth fluoride carbonates with the general formula $\text{NaLnCO}_3\text{F}_2$ ($\text{Ln} = \text{Eu-Lu}$) was synthesized using mild hydrothermal conditions and characterized by single-crystal X-ray diffraction. All nine compounds are isostructural and crystallize in the orthorhombic space group *Pnma*. The pristine quality of single crystals resulted in high-precision crystal structure solutions. The thermal, magnetic, and optical properties were characterized by thermogravimetric analysis, magnetic susceptibility, and single-crystal photoluminescence emission spectroscopy.

Introduction

Many fluoride carbonate materials have recently captured the attention of the scientific community due to their interesting optical properties, such as second harmonic generation, non-linear optical behavior, as well as their magnetic properties.^{1–6} These materials can adopt different structure types ranging from clusters to chains to sheets and to frameworks.⁷ In fluoride carbonate structures, the metal cations typically lie in the same plane as the carbonate anions. According to a review by Grice *et al.*, the classification of fluoride carbonate structure types is rather challenging as carbonate anions do not polymerize, unlike silicates or borates.⁸

In nature, twenty-two fluoride carbonate mineral species have been identified, and seventeen of them contain rare-earth elements. These minerals are typically found in alkaline or granite rocks that were formed either during magmatic events or crystallized out of hydrothermal brines.⁸ Therefore, many synthetic fluoride carbonates have been synthesized using the hydrothermal method. The hydrothermal synthesis method can be divided into three categories according to the synthesis temperature. The mild hydrothermal method is carried out at 100 °C to 230 °C in PTFE liners sealed inside stainless steel autoclaves. The subcritical hydrothermal method can range up to 350 °C, just below the supercritical point of water. Both in mild and subcritical hydrothermal methods, the reaction takes place under autogenous pressure, while the supercritical hydrothermal method takes place at temperatures from 373 °C to 750 °C (or even higher) at pressures determined by a combination of temperature and fill level.^{8–10} The hydrothermal method is well-known for yielding high-quality single crystalline products and, hence, is very popular.^{9, 11–16}

We utilized the mild hydrothermal method to synthesize high quality crystals of nine new rare-earth fluoride carbonates with the general formula $\text{NaLnCO}_3\text{F}_2$ ($\text{Ln} = \text{Eu-Lu}$). Herein, we report the crystal structures determined via single-crystal X-ray diffraction. All nine materials adopt the horváthite (NaYCO_3F_2) mineral¹⁷ structure and crystallize in the orthorhombic space group $Pnma$. The thermal and magnetic properties of phase pure samples of $\text{NaLnCO}_3\text{F}_2$ ($\text{Ln} = \text{Dy-Er}$) were evaluated by thermogravimetric analysis and temperature-dependent magnetic susceptibility measurements. The materials exhibit paramagnetic behavior down to 2 K. The characteristic $4f-4f$ transitions of $\text{NaLnCO}_3\text{F}_2$ ($\text{Ln} = \text{Eu}$ and Tb) were observed by single-crystal photoluminescence (PL) emission spectroscopy.

Experimental

Synthesis

The following materials were used as received without further purification: Anhydrous Na_2CO_3 (Beantown Chemicals, 99.97%), NaF (Alfa Aesar, 99%), $\text{Eu}(\text{NO}_3)_3 \cdot 6(\text{H}_2\text{O})$ (Strem Chemicals, 99.9%), $\text{Gd}(\text{NO}_3)_3 \cdot 5(\text{H}_2\text{O})$ (Thermo Scientific, 99.9%), $\text{Tb}(\text{NO}_3)_3 \cdot 6(\text{H}_2\text{O})$ (Strem Chemicals, 99.9%), $\text{Dy}(\text{NO}_3)_3 \cdot 5(\text{H}_2\text{O})$ (Alfa Aesar, 99%), $\text{Ho}(\text{NO}_3)_3 \cdot 5(\text{H}_2\text{O})$ (Thermo Scientific, 99.9%), $\text{Er}(\text{NO}_3)_3 \cdot 5(\text{H}_2\text{O})$ (Thermo Scientific, 99.9%), $\text{Tm}(\text{NO}_3)_3 \cdot 5(\text{H}_2\text{O})$ (Thermo Scientific, 99.9%), $\text{Yb}(\text{NO}_3)_3 \cdot 5(\text{H}_2\text{O})$ (Thermo Scientific, 99.9%), $\text{Lu}(\text{NO}_3)_3 \cdot 6(\text{H}_2\text{O})$ (Alfa Aesar, 99%).

Nine new rare-earth carbonate fluorides were synthesized using a mild hydrothermal method. The sodium carbonate was dried overnight, and all rare-earth nitrates were stored in a desiccator to prevent hydration. The starting reagents Na_2CO_3 (2.0 mmol), NaF (1.2 mmol), and $\text{Ln}(\text{NO}_3)_3 \cdot x(\text{H}_2\text{O})$ ($\text{Ln} = \text{Eu-Lu}$, 0.4 mmol) were added to a 23 mL PTFE liner along with 5.0 mL of deionized water. The PTFE liners were sealed inside stainless-steel autoclaves and placed inside a programmable oven. For $\text{Ln} = \text{Eu-Dy}$, the oven was ramped to 220 °C and allowed to dwell for 3 days. For $\text{Ln} = \text{Ho-Lu}$, the oven was ramped to 180 °C and allowed to dwell for 5 days. In all cases, the oven was slow cooled to room temperature at a rate of 3 °C/h. The products were isolated using vacuum filtration, washed with acetone, and air-dried. Phase pure products were obtained for Dy, Ho, and Er analogs only (Figure 1), however, high quality single crystals were obtained in all cases.

Powder X-ray Diffraction (PXRD)

Powder X-ray diffraction (PXRD) data were collected on ground polycrystalline samples to confirm phase purity (Figure 1). Data were collected on a Bruker D2 PHASER diffractometer using $\text{Cu K}\alpha$ radiation over a 2θ range of 5–65° with a step size of 0.02°.

Table 1. Crystallographic data for NaLnCO₃F₂. (Ln = Eu-Ho)

Chemical formula	NaEuCO ₃ F ₂	NaGdCO ₃ F ₂	NaTbCO ₃ F ₂	NaDyCO ₃ F ₂	NaHoCO ₃ F ₂
Formula weight	272.96	278.25	279.92	283.50	285.93
Crystal shape/color	Needle/colorless	Needle/colorless	Needle/colorless	Needle/pale pink	Needle/pink
Crystal system	Orthorhombic				
Space group, Z	<i>Pnma</i> , 4				
a, Å	6.40560(10)	6.38230(10)	6.35560(10)	6.32590(10)	6.30960(10)
b, Å	7.12440(10)	7.09260(10)	7.0583(2)	7.01180(10)	6.99550(10)
c, Å	9.2497(2)	9.2314(2)	9.2049(2)	9.1894(2)	9.1686(2)
V, Å ³	422.120(13)	417.879(13)	412.929(16)	407.605(12)	404.691(12)
ρ_{calcd} , g/cm ³	4.295	4.423	4.503	4.620	4.693
Radiation (λ , Å)	MoK α , 0.71073				
μ , mm ⁻¹	14.904	15.917	17.173	18.379	19.598
F(000)	488.0	492.0	496.0	500.0	504.0
Temperature (K)	298	301	299	299	299
Crystal dim., mm ³	0.03 $\times$ 0.02 $\times$ 0.02	0.10 $\times$ 0.10 $\times$ 0.02	0.06 $\times$ 0.05 $\times$ 0.02	0.08 $\times$ 0.08 $\times$ 0.02	0.08 $\times$ 0.07 $\times$ 0.02
2 θ range, deg.	7.22–56.59	7.246–56.568	7.276–56.622	7.31–66.282	7.328–56.524
Reflections collected	20968	21438	18992	25426	20492
Data/restraints /parameters	567/0/47	558/0/47	557/0/46	824/0/47	543/0/47
R_{int}	0.0257	0.0292	0.0379	0.0249	0.0227
Goodness of fit	1.085	1.241	1.225	1.198	1.260
R ₁ (I > 2 σ (I))	0.0086	0.0061	0.0186	0.0096	0.0067
wR ₂ (all data)	0.0199	0.0147	0.0517	0.0246	0.0175
Largest diff. peak/hole, e $\cdot$ Å ⁻³	0.52/–0.54	0.28/–0.28	1.05/–1.55	0.63/–0.50	0.50/–0.31

Table 2. Crystallographic data for NaLnCO₃F₂. (Ln = Er-Lu)

Chemical formula	NaErCO ₃ F ₂	NaTmCO ₃ F ₂	NaYbCO ₃ F ₂	NaLuCO ₃ F ₂
Formula weight	288.26	289.93	294.04	295.97
Crystal shape/color	Needle/pink	Needle/colorless	Needle/colorless	Needle/colorless
Crystal system	Orthorhombic			
Space group, Z	<i>Pnma</i> , 4			
a, Å	6.28710(10)	6.26630 (10)	6.2476(2)	6.22850(10)
b, Å	6.96330(10)	6.92920(10)	6.8989(2)	6.87500(10)
c, Å	9.1526(2)	9.1412(2)	9.1259(2)	9.1192 (2)
V, Å ³	400.691(12)	396.915(12)	393.341(19)	390.493(12)
ρ_{calcd} , g/cm ³	4.778	4.852	4.965	5.034
Radiation (λ , Å)	MoK α , 0.71073			
μ , mm ⁻¹	20.992	22.401	23.865	25.330
F(000)	508.0	512.0	516.0	520.0
Temperature (K)	298	298	298	298
Crystal dim., mm ³	0.09 $\times$ 0.06 $\times$ 0.02	0.07 $\times$ 0.06 $\times$ 0.02	0.06 $\times$ 0.06 $\times$ 0.01	0.04 $\times$ 0.04 $\times$ 0.02
2 θ range, deg.	7.354–66.306	7.38–66.252	7.404–56.666	7.424–56.588
Reflections collected	27791	39806	19970	19901
Data/restraints /parameters	816/0/47	806/0/47	535/0/46	528/0/47
R_{int}	0.0293	0.0274	0.0218	0.0232
Goodness of fit	1.175	1.260	1.242	1.219
R ₁ (I > 2 σ (I))	0.0086	0.0083	0.0065	0.0059
wR ₂ (all data)	0.0212	0.0206	0.0172	0.0155
Largest diff. peak/hole, e $\cdot$ Å ⁻³	0.80/–0.67	0.70/–0.63	0.46/–0.33	0.30/–0.38

Single Crystal X-ray Diffraction (SXRD)

Single-crystal X-ray diffraction data were collected at 298-301 K on a Bruker D8 QUEST diffractometer equipped with an Incoatec I μ S 3.0 microfocus radiation source (MoK α , λ = 0.71073 Å) and a PHOTON II area detector. The crystals were mounted on a microloop using immersion oil. The raw data reduction and absorption corrections were performed using SAINT and SADABS programs.¹⁸ Initial structure solutions were obtained with SHELXT¹⁹ using intrinsic phasing and the Olex2 GUI.²⁰ Full-matrix least-square refinements against F^2 were performed with SHELXL-2018 software.²¹ The crystallographic data and results of the diffraction experiments are summarized in Tables 1 and 2.

Thermogravimetric Analysis (TGA)

TGA measurements were performed on polycrystalline powder samples using an SDT Q600 Thermogravimetric Analyzer and an alumina pan as the sample holder. Samples were heated from room temperature to 800 °C at 10 °C/min under a flow of nitrogen gas (100 mL/min) (Figure 4).

Magnetic Measurements

Magnetic susceptibility measurements of NaLnCO₃F₂ (Ln = Dy-Er) were performed using a Quantum Design MPMS3 SQUID magnetometer. Susceptibility measurements were performed using an applied field of 0.1 T in the temperature range of 2–300 K. All magnetic data were corrected for radial offset and shape effects.²²

Photoluminescence Measurements

Photoluminescence (PL) emission spectra were collected on single crystals of NaEuCO₃F₂ and NaTbCO₃F₂ using a HORIBA Scientific Standard Microscope Spectroscopy Systems connected with iHR320 Spectrometer and Synchrony detector operating on Labspec 6 software. Spectra were recorded from 400 to 750 nm using 375 nm laser excitation source power 0.5 mW with 10 $\times$ UV objective.

Results and Discussion

Synthesis

Synthesis of complex rare-earth fluorides via mild hydrothermal methods has always been challenging due to the immediate precipitation of binary rare-earth fluorides, typically LnF_3 , especially if the reaction involves $\text{HF}(\text{aq})$. However, the addition of chelating agents, such as carbonates/oxalates, results in the complexation of rare-earth cations, which slows down the immediate fluorination and precipitation.²³ Furthermore, the introduction of carbonates into the reaction facilitates the crystal growth of ternary/quaternary rare-earth fluorides, as they can adopt crystal structures similar to naturally occurring minerals.⁸

In this work, we applied a similar reaction profile as utilized by Luo *et al.* to synthesize $\text{Na}_8\text{Lu}_2(\text{CO}_3)_6\text{F}_2$ and $\text{Na}_3\text{Lu}(\text{CO}_3)_2\text{F}_2$.²⁴ In our attempts to resynthesize these phases, we however, obtained single crystals of $\text{NaLuCO}_3\text{F}_2$ instead when performing the reaction at 180 °C. According to Luo *et al.*, the reactions were run at 180 °C, and the starting reagents were pre-dissolved in water before loading the reactions into the oven.²⁴ Skipping the pre-dissolving step of starting reagents may have led to our different outcome. During this study, we were able to obtain phase-pure samples of the $\text{NaLnCO}_3\text{F}_2$ ($\text{Ln} = \text{Dy-Er}$) compositions (Figure 1). The remaining phases were often mixed with unknown phases or impurities, such as rare-earth oxyfluorides. The $\text{Na}_2\text{CO}_3\text{-YF}_3\text{-H}_2\text{O}$ ²⁵ and $\text{Na}_2\text{CO}_3\text{-YbF}_3\text{-H}_2\text{O}$ ²⁶ phase diagrams at 190 °C reported by Ali *et al.* illustrate the sensitivity of the reagent ratios and the water content. Five different fluoride carbonates with similar formula and structure relations are observed in both phase diagrams.⁸ As mild hydrothermal synthesis is prone to trap kinetic phases at low temperatures, the existence of multiple phases in post-reaction products is to be expected.

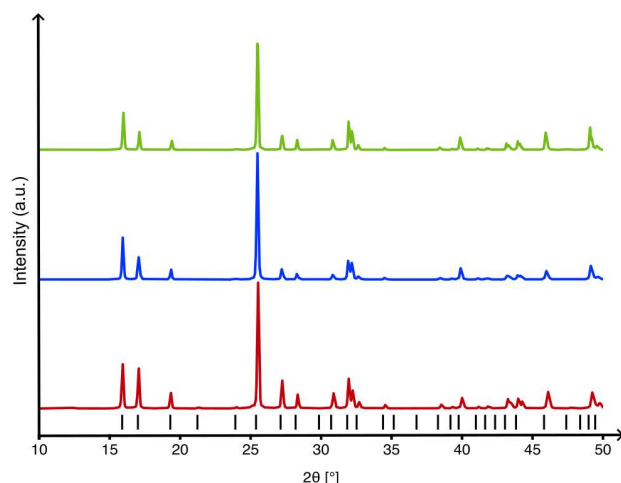


Figure 1. PXRD data for $\text{NaLnCO}_3\text{F}_2$ ($\text{Ln} = \text{Dy}(\text{green})$, $\text{Ho}(\text{blue})$, and $\text{Er}(\text{red})$). The black lines are calculated Bragg peaks from CIF.

In the process of expanding the $\text{NaLnCO}_3\text{F}_2$ series by incorporating different rare-earth cations, we observed that in order to obtain single crystals of $\text{NaLnCO}_3\text{F}_2$ ($\text{Ln} = \text{Eu-Dy}$), we had to increase the reaction temperature to 220 °C. According to a review by Grice *et al.*, it is noted that mid-lanthanide (Eu and Gd) fluoride carbonates require synthesis temperatures around 190–700 °C, and early lanthanide fluoride carbonates require about 700 °C and supercritical synthesis conditions.⁸ Due to the thermal limitations of the PTFE liners used in the synthesis, we could not run reactions above 230 °C. Thus, we were unable to expand the series to obtain the early lanthanide (La-Sm) phases. In addition, La^{3+} - Sm^{3+} cations have larger ionic radii with respect to the late lanthanide cations (Eu^{3+} - Lu^{3+}). Therefore, the early lanthanide containing phases may adopt a different crystal structure type than the observed phases.

Crystal Structure Description

All nine compounds crystallize in the centrosymmetric space group $Pnma$ in the orthorhombic crystal system (Figure 2a). The asymmetric unit consists of one europium atom, a sodium atom, a fluorine atom, a carbon atom, and 3 oxygen atoms. Except for the fluorine atom on Wyckoff site 8d (site symmetry 1), the remaining atoms reside on Wyckoff site 4c (site symmetry .m.). All structure solutions were obtained with excellent R_1 -values ranging from 0.59% to 1.86% (Tables 1 and 2), indicating the pristine quality of the single crystals synthesized. These materials are isostructural with the naturally existing mineral horváthite (NaYCO_3F_2).¹⁷ The crystal structure for $\text{NaYbCO}_3\text{F}_2$ analog was previously reported by Ali *et*

al. with an R_I -value of 3.0%²⁷. They obtained single crystals of $\text{NaYbCO}_3\text{F}_2$ via a microwave reaction instead of via the mild hydrothermal route. Herein, we report the crystal structure solutions for 9 compositions, including the redetermination of the structure of $\text{NaYbCO}_3\text{F}_2$ with an excellent R_I -value of 0.65% (Table 2).

The crystal structure of $\text{NaLnCO}_3\text{F}_2$ is built-up from eight coordinated Ln centered polyhedra, with 4 fluorine atoms and 3 carbonate molecules bound to the rare-earth atom (Figure 2b). These polyhedra are connected to each other by edge-sharing via fluorine atoms and form chains along the b -axis (Figure 2c). These chains are connected via the carbonate molecules, resulting in a 3-dimensional channel structure; the sodium atoms reside within the channels.

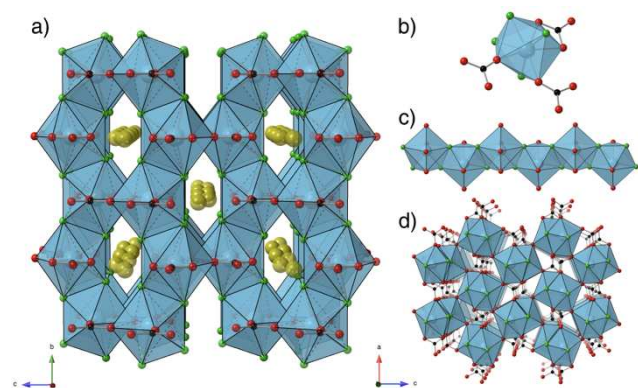


Figure 2. (a) View on the crystal structure of $\text{NaLnCO}_3\text{F}_2$ ($\text{Ln} = \text{Eu-Lu}$) on the bc plane. (b) $\text{Ln}(\text{CO}_3)_3\text{F}_4$ coordination polyhedron. (c) $[\text{Ln}(\text{CO}_3)_3\text{F}_4]_n$ chain. (d) View on the crystal structure of $\text{NaLnCO}_3\text{F}_2$ on the ac plane. Na, Ln, C, O, and F atoms are shown in yellow, blue, black, red, and green color spheres, respectively.

As expected, due to the lanthanide contractions, we observed that the unit cell volume decreases linearly from the Eu to the Lu analog. The measured unit cell volume was plotted against the cubed ionic radii of the rare-earth atoms in an eight-coordinate environment (Figure 3). The ionic radii were obtained from the Shannon ionic radii database.²⁸ It is important to note that despite the lanthanide contraction, all materials adopt the same crystal structure. This demonstrates the tunability of the crystal structure to accommodate different cations.

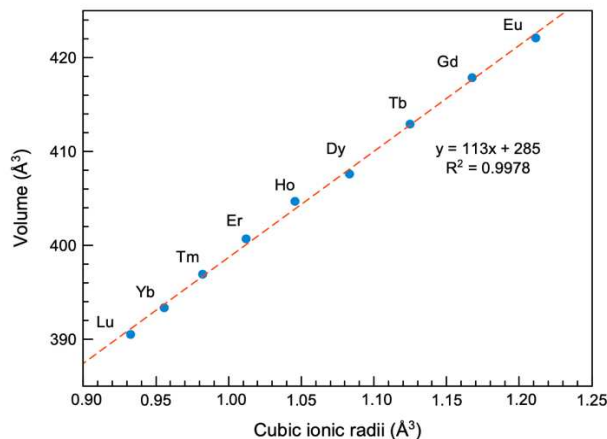


Figure 3. Unit cell volume vs. rare-earth cubic ionic radii plot.

Thermal Properties

Thermogravimetric analysis was performed for the phase pure materials of $\text{NaLnCO}_3\text{F}_2$ ($\text{Ln} = \text{Dy-Er}$). See Figure 4. The materials undergo thermal decomposition around 350–400 °C and form rare-earth oxyfluorides and sodium fluoride. For all materials, the weight loss was around 16%, corresponding to the loss of a molecule of CO_2 .²⁴ The decomposition reaction can be written as follows: $\text{NaLnCO}_3\text{F}_2(\text{s}) \rightarrow \text{LnOF}(\text{s}) + \text{NaF}(\text{s}) + \text{CO}_2(\text{g})$

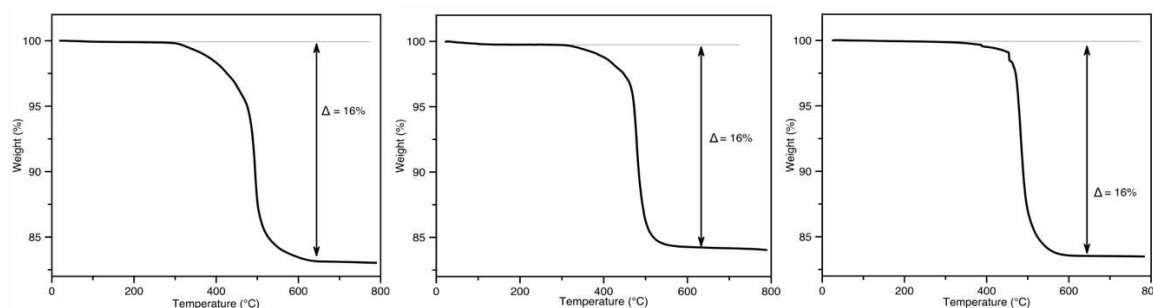


Figure 4. TGA plots for $\text{NaLnCO}_3\text{F}_2$ ($\text{Ln} = \text{Dy}$ (left), Ho (middle), and Er (right)).

Magnetic Properties

We pursued magnetic measurements of the phase-pure samples due to the interesting connectivity of rare-earth cations in the structure. However, the materials $\text{NaLnCO}_3\text{F}_2$ ($\text{Ln} = \text{Dy-Er}$) did not display long range magnetic order and exhibited paramagnetic behavior down to 2 K. The materials follow the Curie-Weiss behavior with small Weiss constants (Figure 5). The magnetic data for $\text{NaLnCO}_3\text{F}_2$ ($\text{Ln} = \text{Dy-Er}$) are summarized in Table 3. The observed magnetic moments agree well with the calculated moments for all materials. According to the literature,

many rare-earth fluoride carbonates do not exhibit long-range magnetic order due to weak $4f-4f$ magnetic interactions.⁸

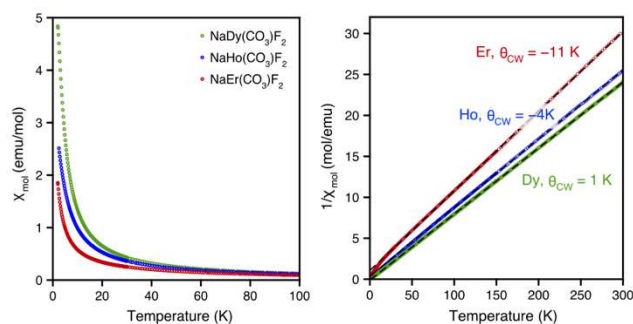


Figure 5. Magnetic susceptibility vs. temperature plot (left) and inverse magnetic susceptibility vs. temperature plot, the Curie-Weiss fit is shown in black dashed lines (right).

Table 3. Magnetic Properties (4-6).

Compound	Magnetic properties	Effective magnetic moment (μ_{eff}) ($\mu_B/\text{F.U.}$)		θ_{CW} (K)
		observed	calculated	
$\text{NaDyCO}_3\text{F}_2$ (4)	Paramagnetic	9.97	10.63	1
$\text{NaHoCO}_3\text{F}_2$ (5)	Paramagnetic	9.77	10.60	-4
$\text{NaErCO}_3\text{F}_2$ (6)	Paramagnetic	9.06	9.59	-11

Photoluminescence Properties

Single-crystal PL emission spectra were collected for the $\text{NaErCO}_3\text{F}_2$ and $\text{NaTbCO}_3\text{F}_2$ materials. Both exhibit characteristic $4f-4f$ electronic transitions as illustrated in Figure 6. For $\text{NaErCO}_3\text{F}_2$, the PL emission is dominated by the $\text{Eu}^{3+} {}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition, consistent with the observed red luminescence. The spectrum also consists of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition, i.e., the magnetic dipole transition. The presence of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ transition indicates that Eu^{3+} occupies a site with C_{nv} , C_n , or C_s symmetry which agrees with the site symmetry(.m.) determined via the crystal structure solution.^{29, 30}

Unlike the europium analog, $\text{NaTbCO}_3\text{F}_2$ exhibits broad peaks at 490 nm, 541 nm, 585 nm, and 622 nm, corresponding to ${}^5\text{D}_4 \rightarrow {}^7\text{F}_6$, ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$, ${}^5\text{D}_4 \rightarrow {}^7\text{F}_4$, and ${}^5\text{D}_4 \rightarrow {}^7\text{F}_3$ transitions, respectively (Figure 6). The ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$ transition at 541 nm dominates the PL emission spectrum, resulting in a green-colored luminescence that agrees well with previously reported Tb-doped materials.³⁰⁻³²

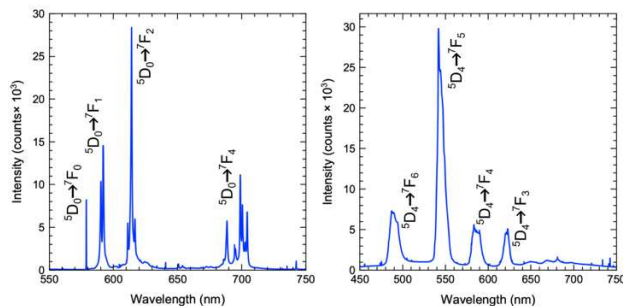


Figure 6. Photoluminescence emission spectra for NaEuCO₃F₂ (left) and NaTbCO₃F₂ (right).

Conclusion

High-quality single crystals of nine new rare-earth fluoride carbonates with the general formula NaLnCO₃F₂ (*Ln* = Eu–Lu) were synthesized via mild hydrothermal synthesis. The single crystals of Ho–Lu analogs were synthesized at 180 °C, while higher temperatures were required to obtain single crystals of the Eu–Dy analogs. The pristine quality of the single crystals was demonstrated by the extremely small *R*₁ values obtained for the crystal structure solutions ranging from 0.59% to 1.86%. The materials undergo thermal decomposition at 350–400 °C and decompose into rare-earth oxyfluoride and sodium fluoride, releasing carbon dioxide. Magnetic susceptibility measurements revealed that the materials are paramagnetic down to 2 K, and europium and terbium analogs exhibited characteristic *4f–4f* transitions in single-crystal photoluminescence emission spectra. This work further illustrates the capability of mild hydrothermal synthesis for obtaining complex rare-earth fluorides at low temperatures. Utilizing other complexing agents, such as oxalates or borates, may lead to the discovery of new mixed anion rare-earth fluoride materials with interesting properties.

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Accession Codes

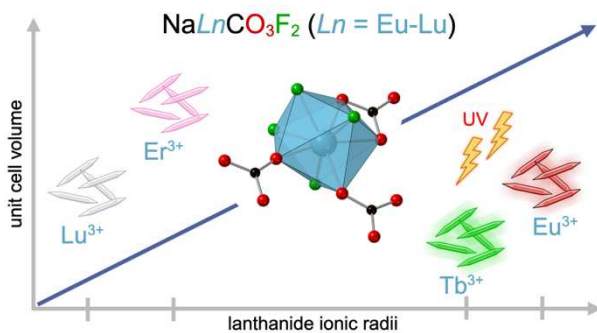
CCDC **2360924–2360932** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Synopsis

Nine new isostructural rare-earth fluoride carbonates were synthesized using mild hydrothermal synthesis. Their crystal structure and magnetic, thermal, and optical properties are discussed.