Synthesis, crystal structures and luminescence properties of rare earth-cadmium hydroxycarbonats with the formula $RE_2Cd(CO_3)(OH)_6$ (RE = Y, Er)

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ABSTRACT

We report on the synthesis and crystal structures of two rare earth-cadmium hydroxycarbonats, namely, $RE_2Cd(CO_3)(OH)_6$ (RE = Y, Er). Two new rare earth-cadmium hydroxycarbonates are isostructural. They both exhibit 3D complicated network based on REO_8 and CdO_6 polyhedra, which are connected by CO_3 triangle unit via corner-sharing or edge-sharing. $RE_2Cd(CO_3)(OH)_6$ has a high RE^{3+} concentration (1.05×10^{22}, 1.06×10^{22} ions/cm^3 for **Y** and **Er**, respectively). IR, UV–vis spectra, thermogravimetric analysis (TGA) and luminescence properties of two compounds were also studied. Both compounds are thermally stable up to around 300 °C. In addition, the absorption and emission spectra of two compounds were measured at room temperature, $Y_2Cd(CO_3)(OH)_6$ exhibited a blue fluorescent emission peak at 418 nm with a shoulder at 437 nm (λ_{ex} = 365 nm) in the solid state.

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1. Introduction

Rare-earth and transition-metal heterometallic complexes have drawn more and more attention due to their potential applications in catalysis [1–2], luminescent materials [3–4], sensors [5–7], and magnetism [8] etc. These d–f heterometallic coordination complexes probably show better physical properties compared with the monometallic compounds such as luminescent and magnetic performance [9–12]. Currently, it is still a great challenge to prepare d–f heterometallic coordination frameworks because of the variable and high coordination configurations of lanthanide ions as well as the competitive reactions between lanthanide and transition metals [12]. Therefore, d–f heterometallic complexes are still rare, especially, 4d–4f heterometallic coordination complexes. To date, 4d–4f metal–organic compounds with open frameworks (MOF) such as Ln(III)–Ag(I) (Ln = Sm, Eu, Gd, Tb, Dy, Ho, Y, Yb) and Ln(III)–Cd (Ln = Sm, Eu, Gd, Tb, Dy) [12–13] are supposed to be a very promising class of luminescent materials. Similar with MOF luminescent materials, inorganic compounds of the rare-earth family have also been widely used as luminescent materials, such as $[KLn(SO_4)_2H_2O]$ (Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er) with unusually high thermal stability [14]. A series of heterometallic

Ln(III)–K(I) sulfate and oxalate coordination polymers, namely, $[KLn(ox)(SO_4)(H_2O)]$ (ox = oxalate, Ln = Eu, Tb and Dy) exhibit excellent chemical stability and tunable luminescence, which have been prepared by Du's group [15]. In addition, rare-earth oxycarbonates [16], borates [17] and carbonates have been broadly applied in the hosts of phosphors [21]. It is necessary to improve new luminescent materials due to the brightness problem and the color purity of the current phosphors to satisfy the requirement for application in the color plasma display panels [16–20]. As far as we know, lanthanum hydroxycarbonates have rarely been investigated, a series of $RECO_3(OH)$ (RE = Y, La, Pr, Sm, Eu,) nanomaterial with different morphologies and fluorescence properties have been studied, [21–23] however, 4d–4f heterometallic carbonates are less reported and remain a challenge to chemists [21–23]. In addition, rare earth ions doped inorganic phosphors have been paid much attention because of their unique luminescent properties and applications, yttrium oxides possessing excellent optical and physicochemical properties have been selected as host materials for display application. Thus, here, for the exploration of new rare earth carbonates with good properties, we prepared rare earth-transition-metal hydroxycarbonates through a facile hydrothermal method. In this paper, two new compounds, namely, $Y_2Cd(CO_3)(OH)_6$ and $Er_2Cd(CO_3)(OH)_6$, were discovered, their crystal structures, optical properties, thermal stability and luminescence properties were also studied.

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2. Experimental

2.1. Materials and methods

All reagents were purchased from Shanghai Reagent Factory (AR, 99.0%) and used without further purification. IR spectra were recorded on a WQF-600N spectrometer as KBr pellets in the range of 4000–450 cm^{-1} with a resolution of 2 cm^{-1} at room temperature. Microprobe elemental analyses were performed on a field-emission scanning electron microscope (Hitachi S-4800) equipped with an energy-dispersive X-ray spectroscope (EDS, Oxford INCA). Thermogravimetric analysis (TGA) experiments were carried out a TGA/1100SF instrument at a heating rate of 10 °C/min under nitrogen atmosphere. Optical diffuse reflectance and UV spectra were measured at room temperature with a Shimadzu UV-3600 spectrophotometer and a BaSO$_4$ plate was used as a standard (100% reflectance). The absorption spectra were calculated from reflectance spectra using the Kubelka–Munk function: $\alpha/S = (1 - R)^2/2R$, where α is the absorption coefficient, S is the scattering coefficient (which is practically wavelength independent when the particle size is larger than 5 μm), and R is the reflectance [22]. X-ray powder diffraction (XRD) patterns were collected on a Bruker D8 X-ray diffractometer using Cu Kα radiation in the angular range of 2θ = 5–80° with a step size of 0.1°. The static PL excitation and emission spectra were recorded on a QM/TM fluorescence spectrophotometer. Microprobe elemental analyses for the Y, Er, Cd and O elements were performed on a field-emission scanning electron microscope (FESEM, JSM6700F) equipped with an energy-dispersive X-ray spectroscope (EDS, Oxford INCA).

2.2. X-ray crystallography

X-ray diffraction data collection for RE$_2$Cd(CO$_3$)(OH)$_6$ was performed on a Rigaku Mercury CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å) at 293(2) K. The data sets were corrected for Lorentz and polarization factors as well as absorption by the multi-scan method [24]. The structure was solved by the direct method and refined by full-matrix least-squares fitting on F^2 by SHELX-97 [25]. All non-hydrogen atoms were refined with anisotropic thermal parameters. According to the charge balance and bond valence calculations, six H atoms in RE$_2$Cd(CO$_3$)(OH)$_6$ were assigned to O–H bonds, however, they were not refined due to the difficulty in the determination of their precise locations. And the structure was also checked for possible missing symmetry with PLATON. Crystallographic data and structural refinements are summarized in Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters, important bond distances and angles are listed in Tables S1–S3, respectively. Further details of the crystal structure studies could be obtained from the FIZ Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: (49) 7247808666; E-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD 430504 and 430522 for Y$_2$Cd(CO$_3$)(OH)$_6$ and Er$_2$Cd(CO$_3$)(OH)$_6$, respectively.

2.3. Synthesis

2.3.1. Synthesis of RE$_2$Cd(CO$_3$)(OH)$_6$

Y$_2$O$_3$ or Er$_2$O$_3$ (0.347 g or 0.574 g, 1.5 mmol), Cd(NO$_3$)$_2$·4H$_2$O (0.359 g, 1.2 mmol) and K$_2$CO$_3$ (0.708 g, 5.1 mmol) were mixed in H$_2$O (10.0 mL) and sealed in an autoclave equipped with a Teflon liner (20 mL) and heated at 210 °C for 4 days. The initial and final pH values are 1.5 and 1.0, respectively. The colorless or pink prism-shaped RE$_2$Cd(CO$_3$)(OH)$_6$ crystals were obtained in a yield of ca. 65% or 60% based on Y and Er, respectively. The experimental X-ray powder diffraction pattern is in agreement with the

Table 1
Crystal data and structural refinement for RE$_2$Cd(CO$_3$)(OH)$_6$ (RE = Y, Er).

Compound	1	2
Empirical formula	Y$_2$CdCO$_3$(OH)$_6$	Er$_2$CdCO$_3$(OH)$_6$
Formula weight	452.28	608.98
T (K)	293(2)	293(2)
λ (Å)	0.71073	0.71073
Crystal system	orthorhombic	orthorhombic
Space group	Pnnm	Pnnm
a (Å)	12.1637(8)	12.1543(12)
b (Å)	7.2680(3)	7.2362(6)
c (Å)	8.6282(5)	8.6131(8)
V (Å^3)	762.78(7)	757.53(12)
Z	4	4
D_c (g cm^{-3})	3.938	5.340
μ (Mo Kα)/mm^{-1}	17.875	24.758
$F(000)$	840	1072
Reflections collected/ unique (R_{int})	2548/830 (0.0338)	4206/926 (0.0403)
Completeness	99.5% to theta = 26.36	99.0% to theta = 27.48
Data/restraints/parameters	830/0/67	926/6/68
Goodness-of-fit (GOF) on F^2	1.061	1.181
Final R indices [$I > 2\sigma(I)$]^a	$R_1 = 0.0274$, $wR_2 = 0.0605$	$R_1 = 0.0333$, $wR_2 = 0.0892$
R indices (all data)	$R_1 = 0.0320$, $wR_2 = 0.0631$	$R_1 = 0.0365$, $wR_2 = 0.0914$
Extinction coefficient	0.0036(7)	0.0056(4)
Largest difference peak and hole (e Å^{-3})	1.016 and −0.782	1.926 and −2.484

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $\omega R_2 = \{\Sigma\omega[(F_o)^2 (F_c)^2]^2/\Sigma\omega[(F_o)^2]^2\}^{1/2}$.

simulated diffraction data form the single-crystal crystallographic data (See Supplementary Fig. S1) and the EDS analysis of RE$_2$Cd(CO$_3$)(OH)$_6$ confirms the Y/Er/Cd/O elemental composition (Fig. S2). IR data (KBr cm^{-1}): 3481 (vs), 1630 (m), 1508 (vs), 1387 (s), 1095 (w), 812 (w), 738 (w), 683 (w), 614 (w) for compound 1, 3481 (vs), 1630 (m), 1508 (vs), 1387 (s), 1095 (w), 850 (m), 712 (m), 687 (s), 587 (m) for compound 2, respectively.

3. Results and discussion

3.1. Crystal structure

Compounds 1 and 2 are isostructural, hence only the structure of 1 will be discussed in details as a representative. Y$_2$Cd(CO$_3$)(OH)$_6$ crystallizes in the orthorhombic space group Pnnm (No. 58) and features a three dimensional framework consisting of corner-shared and edge-shared YO$_8$ and CdO$_6$ polyhedra (Fig. 1a). The asymmetric unit of RE$_2$Cd(CO$_3$)(OH)$_6$ includes nine independent non-H atoms, including one Y, one Cd, one C and six O atoms. Y (1) is eight coordinated by six oxygens from six hydroxyl anions and two oxygens from two carbonate anions in a distorted dodecahedral geometry, Cd(1) is six coordinated by five oxygens from five hydroxyl anions and one oxygen from one carbonate anion in a distorted octahedral geometry. The Y–O and Cd–O distances range from 2.333(10) to 2.91(2) Å, and 2.217(5) to 2.571 (5) Å, respectively, comparable to those reported for other Y and Cd oxides [26]. The C(1) atom is coordinated by three O atoms, forming a planar triangle unit with C–O bond lengths and angels of 1.2816(5) to 1.294(9) Å, 118.1 (4)° to 123.8 (7)°, respectively. Each CO$_3$ anion shows a μ_3-$\eta^1\eta^1\eta^3$-coordination mode (5.113) that bridges and chelates one Cd and two Y atoms (Scheme 1). The interconnection of YO$_8$ dodecahedra via edge-sharing oxygen atoms results in a 2D layer in the bc-plane (Fig. 1b), furthermore, CdO$_6$ polyhedra (Fig. 1c) bridge the above 2D layer by corner-sharing and edge-sharing oxygen atoms to yield a 3D framework in the ab plane (Fig. 1a). RE$_2$Cd(CO$_3$)(OH)$_6$ have a high RE^{3+} concentration