

Study of the Structure and the Luminescence Properties of the Tb Compound

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ABSTRACT A lanthanide-organic frameworks $Tb(C_2O_4)(HCOO)$ (**1**) is synthesized via hydrothermal methods at 200 °C. Obtained single crystals are characterized by elemental analysis (EA), powder XRD diffraction SCPXRD, also optical characteristics were categorized by photoluminescence (PL) experiments. The results showed crystals are pure and they exhibit the peak of crystalline orthorhombic *Pnma* group space. The PL emission spectrum has been monitored at 325 nm (pulsed laser He-Cd). Resulted green luminescence spectrum for the green luminescence emission for compound **1** was located at 54.4 nm attributed to ($^5D_0 \rightarrow ^7F_0$) electronic state level. The noticeable intensity of the compound **1** indicated that the lanthanide organic frameworks are good candidate materials for electro-optical devices, field emission displays (FEDs) and they have a potential application in solid-state light.

Keywords: Lanthanide organic framework, photoluminescence, hydrothermal method, single crystal, rare earth.

1 INTRODUCTION

Lanthanide-organic frameworks (LOFs) are certain types of interested materials in field of sensitive devices, biology, chemistry, medicine, and optoelectronics like optical displays panels and light-emitting diodes (LEDs) special chemical and physical properties (Zhang et al., 2008, 2011; Feng et al., 2010; Dai et al., 2010). Hybrid frameworks are composed establishing an extensive period of physical phenomena, for instance photo sensitive, (Du et al., 2007; Lan et al., 2012). Stimulated emission (Sonnur et al., 2011; Gandara et al., 2013) or effects (Weilang et al., 2014 and Ei et al., 2011). In addition, the cooperative functionalities of permanent porosity and luminescence property qualified luminescent MOFs as a very attractive new class of sensing materials. (Hatanaka et al., 2017; Rossin et al., 2012; Dui Efi et al., 2011).

Trivalent lanthanide Ln(III) ions produce attractive optical properties. Recently the luminance studies of rare earths metals that are synthesized with various organic ligands have been conducted. Ln(III) chelates provide narrow band emissions and very pure luminescence using UV/VIS excitation (Atva et al., 1997). This sensitized luminescence of the lanthanide compounds are commonly used for the optical materials, biological applications, electroluminescent devices, optical amplifier or laser, and sensors (Bunzli and Piguet, 2005; Cui et al., 2014).

Luminescence of compound Terbium (Tb^{3+}) take the tending due to the narrow f-f transitions of their good sensitization luminescence that can be carried out through the antenna effect as well as the line of emission spectra look mostly sharp as it depends on the crystal field around the metal ions. Furthermore luminescence Tb^{3+} owing the ability acting as phosphors and progress of

materials (Vicentini et al., 2000). It is well-known that comprehensive interest over the past few years because not only their interesting applications but also their luminescence which originated (Robbei Fromm, 2006; Chandler et al., 2016; Gu and Xue, 2016). This specific luminescence is characterization (Gherohe et al., 2006; Zhue et al., 2007; Zirrman et al., 2007).

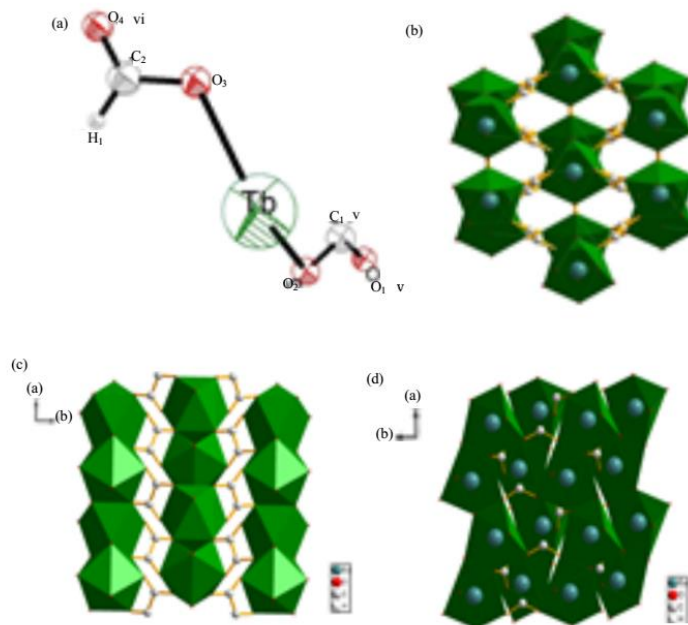


Fig. 1: Illustration of the crystal structure of the $\text{Tb}(\text{C}_2\text{O}_4)(\text{HCOO})$ 1 hybrid framework with asymmetric unit: a) Typical single crystal morphology (habit) and its low index face and b-d) Views perpendicular to the (100), (010) and (001) planes, respectively, hydrogen atoms have been deleted for clarity

Herein we show incorporated material candidates of their wide structural body (Theetham et al., 2006; Rao et al., 2008; Kuromo, 2009; Llanderf et al., 2009; Jain et al., 2008). The synthesized compound **1** was first successfully synthesized by hydrothermal method, where compound **1** and **2** consist of lanthanide organic frameworks prepared by Romero et al.; 2016. In Figure 1, explained the cryst. structure of sample **1**, we can notice that basic bodyg s are the matter M;O;M periodand, namely the oxalate ($\text{C}_2\text{O}_4^{2-}$) and the fornate (HCOO^-), which are largely perpendicular to one another as well, it is known that oxa is body more solid than others.

In the present work, compound **1** is successfully prepared by hydrothermal method, the crystal structure and the optical properties have been described in details. The results showed that compound **1** exhibited strong green luminescence the characteristics luminescence of Tb^{3+} ions indicating that the compound **1** are a perfect experimental probe of the crystalline environment.

2. Materials and methods

2.1 Materials and measurements :Every starting materials and solvents are reagent grade commercially available the materials provided by Aldrich. All materials were used as received without further purification. PXRD patterns for complex **1** was collected on (Empyrean, PANalytical V. V., 40kV, 40 mA) (Cu-Kal)(1.540598Å) range $\theta = 5-80^\circ$. XRD result of **1** were collected at room temperature Diffraction Rigaku. XtalABminTM. EA test was performed Micro Cube. Optical measurements were performed using pulsed laser He-Cd (325 nm) (Horiba Jobin Yvon) at room temperature.

Table 1. Crystallographic data of compound (1).

Compound	1
Formula sum	C₃H₁O₆Tb₁
Formula weight	291.96 g/mole
Crystal System	Orthorhombic
Space-Group	<i>Pnma</i>
Cell Parameters	<i>a</i> = 7.0138(3) Å, <i>b</i> = 10.6077(4) Å <i>c</i> = 6.66021(6) Å
<i>α</i>	90
<i>β</i>	90
<i>γ</i>	90
V(Å³)	491.198
<i>D_c</i>(g cm⁻³)	3.948
<i>Z</i>	4

Table 2. Atomic parameters of compound (1).

Atom	x/a	y/b	z/c
Tb1	0.20372(4)	0.13266(4)	0.25000(4)
O1	-0.0863(5)	0.1464(4)	0.1234(3)
O2	0.2361(5)	-0.0205(6)	0.4562(3)

2. 2 Synthesis of Tb(C₂O₄)(HCOO)

We prepared the Materials have been prepared at 200 ° C for a week, the solution has been heated. Aqueous solution of polychlorinated biphenyls and the change in heating periods and duration, it has been observed that no single crystals were developed. The final product, including of crystals of compound **1** were recovered by filtration, cleaned with water and alcohol.

2. 3 Structure determination

Tables (1, 2) present the results of the compound **1**. Fig. 2 shows the XRD pattern of the as-formed samples through hydrothermal method. Crystallographic data were collected with OXFORD Diffraction Rigaku. XtalABminTM Diffractometer, and all data indicates that the compounds Tb(C₂O₄)(HCOO) are pure and exhibited the peak of pure crystalline orthorhombic group *Pnma* (62), which was well consistent with the created CIF file (XPRT HIGH SCORE PLUS) as shown in Fig. 2 below. Crystallographics is displayed in Tables (1-4) below.

Table 3. Selected geometric information of compound (1).

Atom	U ₁₁	U ₂₂	U ₃₃
Tb1	0.00933(16)	0.00875(14)	0.00791(16)
O1	0.0160(15)	0.0158(13)	0.0098(14)
O2	0.0164(15)	0.0294(18)	0.0162(17)
Atoms 1,2	d 1,2 [Å]	Atoms 1,2	d 1,2 [Å]
Tb1—O1	2.465(3)	Tb1—O3	2.493(4)
Tb1—O1 ⁱ	2.491(3)	Tb1—O3 ⁱ	2.442(5)
Tb1—O1 ⁱⁱ	2.465(3)	Tb1—O4	2.472(5)
Tb1—O1 ⁱⁱⁱ	2.491(3)	O1—C2	1.274(5)
Tb1—O2 ⁱⁱ	2.436(3)	O2—C2 ^v	1.238(5)
Tb1—O2	2.436(3)	C2—C2 ^{iv}	1.545(8)
Tb1—C2 ^{iv}	3.230(4)	O3—C3	1.293(7)
Tb1—C2 ^v	3.230(4)	C3—O4 ^{vi}	1.216(8)

Table 4. Selected bond length(Å) and angles (deg.) for compound (1)

Angle 1, 2, 3 [°]	Angle 1, 2, 3 [°]	Angle 1, 2, 3 [°]	Angle 1, 2, 3 [°]
O1 ⁱⁱ —Tb1— O1	66.56(15)	O3—Tb1—O1 ⁱ	76.57(11)
O1 ⁱⁱⁱ —Tb1— O1	100.38(11)	O3—Tb1—O2 ⁱⁱ	114.33(9)
O1 ⁱⁱ —Tb1— O1 ⁱ	100.38(11)	O3 ⁱ —Tb1— O2 ⁱⁱ	78.52(10)
O1 ⁱⁱⁱ —Tb1— O1 ⁱ	65.75(15)	O3 ⁱ —Tb1—O2	78.52(10)
O2 ⁱⁱ —Tb1— O1	66.32(11)	O3—Tb1—O2	114.33(9)
O2—Tb1— O1 ⁱ	72.49(12)	O3—Tb1—C2 ^{iv}	102.14(9)
O2—Tb1— O1 ⁱⁱⁱ	132.86(11)	O3 ⁱ —Tb1— C2 ^{iv}	97.88(9)
O2 ⁱⁱ —Tb1— O1 ⁱⁱⁱ	72.49(12)	O3 ⁱ —Tb1—C2 ^v	97.88(9)
O2 ⁱⁱ —Tb1— O1 ⁱ	132.86(11)	O3—Tb1—C2 ^v	102.14(9)
O2—Tb1— O1	126.17(12)	O4—Tb1—O1	70.70(12)

O2—Tb1— O1 ⁱⁱ	66.32(11)	O4—Tb1— O1 ⁱⁱⁱ	142.29(9)
O2 ⁱⁱ —Tb1— O1 ⁱⁱ	126.17(12)	O4—Tb1—O1 ⁱⁱ	70.70(12)
O2 ⁱⁱ —Tb1— O2	129.30(19)	O4—Tb1—O1 ⁱ	142.29(9)
O3 ⁱ —Tb1— O1 ⁱ	64.80(11)	C2 ^{iv} —C2—O1	115.1(5)
O3 ⁱ —Tb1— O1 ⁱⁱ	144.72(8)	C2 ^{iv} —C2— O2 ^{viii}	118.7(5)
O3 ⁱ —Tb1— O1	144.72(8)	C3—O3—Tb1	122.3(4)
O3—Tb1— O1 ⁱⁱ	64.46(10)	C3—O3— Tb1 ^{vii}	134.2(5)
O3—Tb1— O1 ⁱⁱⁱ	76.57(11)	O4 ^{vi} —C3—O3	125.6(7)
O3 ⁱ —Tb1— O1 ⁱⁱⁱ	64.80(11)	C3 ^{ix} —O4—Eu1	129.0(5)
O3—Tb1— O1	64.46(10)		

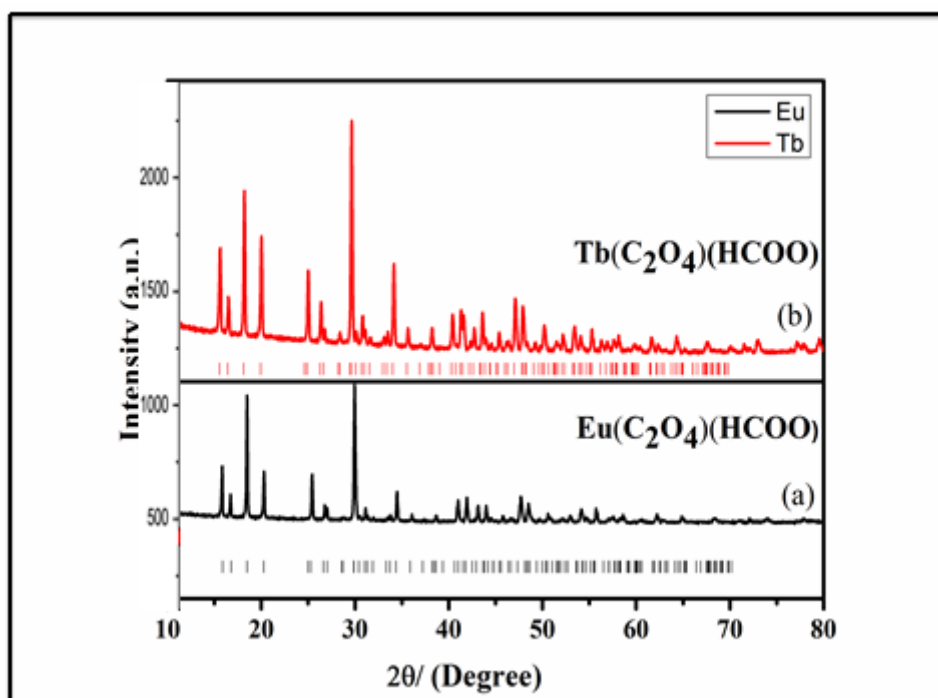


Fig. 2 The PXRD patterns of the $\text{Tb}(\text{C}_2\text{O}_4)(\text{HCOO})$.

RESULTS AND DISCUSSION

Structure description: In this work, the X-ray diffraction of compound 1 as illustrated in Fig.1.

It is also observed that the structure of compound **1** is orthorhombic. The structures of **1** is 3-D hybrid frameworks which are $Pnma(62)$ space group. connectivities chains

Finally, the structures for the two compounds **1** is built up from Eu, Tb oxalate shared all their oxygen atoms with oxalate and formate ligands, thus take the shape of a 3D framework structure as shown

Luminescent property:Photoluminescence experiment results were measured using an excitation wavelength of the pulsed ultraviolet He-Cd laser 325 nm at room temperature. Notably compound **1** show emissions intensity in the range of 300 to 800 nm as displayed in Fig. 3. The emission spectra of compound **1** gave the characteristics of Tb^{+3} transitions, respectively. The resonance energy levels of terbium ions are presented in Table.5 along with the various luminescence transitions.

in Fig. 1.

Fig. 3) illustrates the photoluminescence spectra for compound **1**, there are .The spectrum is dominated by the major sharp peak at 54.4 nm due to $^5D_0 \rightarrow ^7F_9$ transition which give strong emission, as well as the other emission bands are: $^5D_0 \rightarrow ^7F_9$ at 48.0 nm and $^5D_1 \rightarrow ^7F_3$ at 589 nm and $^5D_4 \rightarrow ^7F_3$ at 600 nm, respectively.

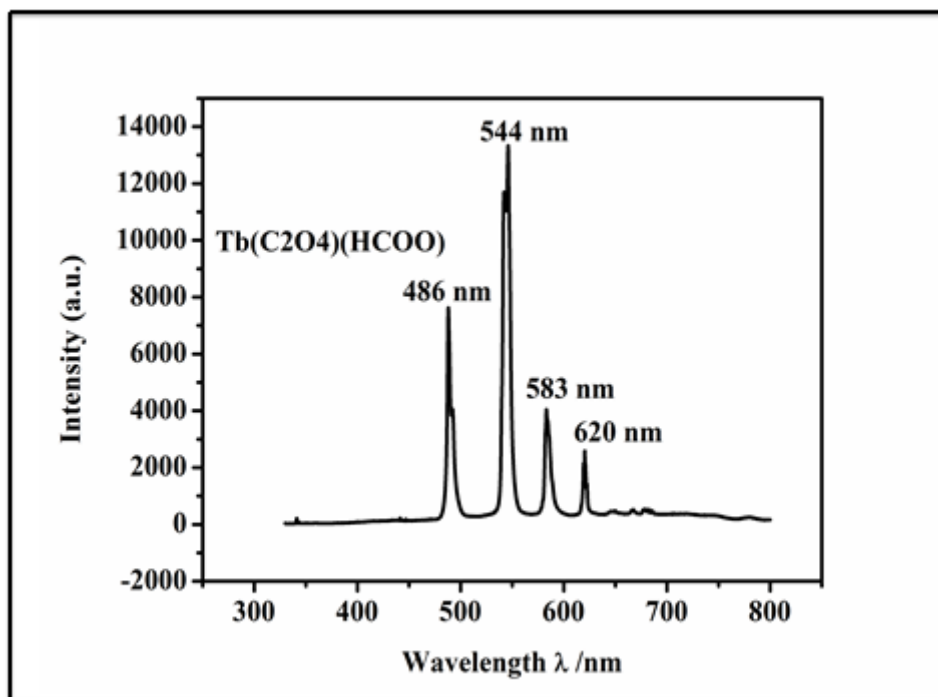


Fig. 3 PL spectra from compound of Tb compound.

Table.5 Energy levels and luminescence transition for Europium(18, 19) and Terbium (20).

Upper energy levels(energy cm^{-1})	Lower levels	λ (nm)
$Tb^{+3} ^5D_3(26250)$	$^7F_6, ^7F_5, ^7F_4, ^7F_3, ^7F_2, ^7F_1, ^7F_0$	490, 545, 587, 622,
$^5D_4(20500)$		650, 671, 681

CONCLUSION

In the presented work, 3-D hybrid framework **1** was successfully prepared through hydrothermal method and measured by SCPXRD. compound **1** has asymmetric unit, and the spectrum of UV laser induced photoluminescence shows that compound **1** gave a strong strong green emission at 54.4 (nm), respectively. Measurements indicate that the luminescence behavior demonstrates that rare earth organic framework (REOFS) of compound **1** has excellent potential application in solid state, field emission displays (FED)

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