

The Study of the Optical Properties of the Lanthanide organic framework

Nada Abdul Hadi Kareem^{1,a}, Nadia Mohammed Jassim^{2,b*}, Jasim Mohammed Mansoor^{3,c},
Muayed kadhim rasheed^{4,d}.

¹Department of Physics, College of Education, University of Al- Qadisiyah, Qadisiya city, Iraq.

^{2,3,4}Department of Physics, College of Science – Daiyla University – Baquba City 32001, Daiyla governorate, Iraq.

Abstract

A new Tb compound consisted of terbium oxalate formate was synthesized by autogenous pressure at a temperature around 200 °C over seven days and we obtained pure single crystals and study both of the structure of the Tb compound and optical properties. The optical measurements were defined by photoluminescence (PL) tests, the PL experiment used pulsed He- Cd 325 nm and the resulted PL spectrum showed green luminescence spectrum emission for the was located at 544 nm attributed to (⁵D₄→⁷F₅) electronic transition. The remarkable PL emission intensity for the specific organic and inorganic compound indicated that the lanthanide organic frameworks are perfect candidate materials for optoelectronic devices, field emission displays (FEDs) and they have a potential application in solid- state light.

Introduction

Trivalent lanthanide ions are fascinating luminescence sources in order to their high color purity and relatively long lifetimes associated to the 4f-shell electronic transitions [1].

They have attracted interest in a wide range of important electronic and biotechnological fields. For instance, emitting complexes of Tb(III) ions is employed as markers in fluoroimmunoassays, where quantitative estimation of antigens in biological matrixes is needed. Because of their strong and long-lived luminescence, the background signal from the biological matrix can be circumvented making the detection of the desired analytical signal particularly easy [2]. 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 [7]. This sensitized luminescence of the lanthanide compounds are commonly used for the optical materials, biological applications, electroluminescent devices, optical amplifier or laser and sensors [8, 9]. Moreover, a new-generation of in vivo imaging technologies requires low frequency light because of its penetration capability through biological tissues. To this end, NIR luminescence from Yb(III), Nd(III), Pr(III), Er(III) and related complexes are particularly attractive. Other relevant practical applications where Ln(III) ions may be involved are related to the optical amplification in laser technology [Nd(III)] or to the production of silica-based fibers for optical networks, where the emission wavelengths of Pr(III) (ca. 1330 nm) and Er(III) (ca. 1550 nm) ions closely match with "windows of transparency" in silica used for telecommunications. [10] Luminescence of compound Terbium (Tb³⁺) take the tending due to the narrow f-f transitions have attracted a lot of attention because 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

a great attention has been paid to the luminescence of Tb^{3+} ions owing to the ability of acting as phosphors and progress of materials [10]. It is well-known that rare earth organic frameworks (REOFs) have attracted comprehensive interest over the past few years because not only their interesting applications but also their luminescence which originated from intra 4f or 4f–5d transitions [11]. This specific luminescence is characterized by, high luminescence quantum yield, narrow bandwidth, long life time, large Stokes shifts, and ligand dependent luminescence sensitization [12].

The frameworks are composed by an organic ligand and a metal ion within a porous structure establishing an extensive range of emissive phenomena, for instance linker-based luminescence, metal-based emission or antennae effects. Both the inorganic and the organic moieties can provide the platforms to produce luminescence, typically the origin of luminescence emission widely observed in lanthanide MOFs via the so-called (antenna effect) which is often referred to as (LMCT), since the strongly absorbing ligand acts as a receiving antenna for the bond metal ion. In addition, the cooperative functionalities of permanent porosity and luminescence property qualified luminescent MOFs as a very attractive new class of sensing materials. [13]

Herein we show crystalline framework materials incorporated both inorganic and organic moieties are attracting candidates because of their wide chemical and structural variety that propose opportunities for making many technologically relevant properties [14]. Notably, the dense hybrid systems usually incorporated with infinite inorganic connectivity, like metal-oxygen-metal (M-O-M) arrays, that present the topological characteristics desired for certain types of physical properties [15]. The synthesized compound **1** was first successfully synthesized by hydrothermal method, where compound **1** and **2** consist of lanthanide organic frameworks with an orthorhombic crystal structure, as previously prepared by Romero et al [16]. In Fig. 1 we illustrated the crystal structure of compound **1**, we can notice that the three basic building blocks are the inorganic M-O-M chains and the two organic bridging ligands, namely the oxalate ($C_2O_4^{2-}$) and the formate ($HCOO^-$) ions, which are effectively oriented perpendicular to one another as well, it is also known that oxalate is structurally more rigid than formate.

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. EXPERIMENTAL

2.1 Materials and measurements

All 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) diffractometer, using (Cu-K α)(1.540598Å) radiation in the angular range $2\theta = 5-80^\circ$. Single crystal X-ray data of **1** were collected at room temperature using OXFORD Diffraction Rigaku. XtalABminTM Diffractometer. EA test was performed using an Elementar Vario Micro Cube ELIII elemental analyzer. Optical measurements were performed using pulsed laser He-Cd (325 nm) (Horiba Jobin Yvon) at room temperature.

2.2 Synthesis of $Tb(C_2O_4)(HCOO)$

We prepared the title compounds was carried out in a Pyrex-lined steel bomb (autogenous pressure) at the temperature around $200C^\circ$ over a period for a week, single crystals were obtained by heating an aqueous suspension of Tb oxalate decahydrate $Tb_2(C_2O_4) \cdot 10H_2O$, 0.5 mmol of Tb oxalate decahydrate and 15 mmol of acid oxalic dihydrate in 10 mL of water for a week. By varying the heating time less or more than 7 days, it has been observed that no single crystals were developed. The final product, consisting of single crystals of compound **1** were recovered by filtration, washed with water and ethanol, and then dried in air.

2.3 Structure determination

Tables (1, 2) present a summary of the crystal data, data collection and refinement parameters for the compound **1**. Fig. 2 shows the XRD pattern of the as-formed samples through hydrothermal method. Crystallographic data were collected with OXFORD Diffractometer, XtaLABmini™ 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 and the selected, bond lengths and angles are listed in Tables (1-4) below.

3 RESULTS AND DISCUSSION

3.1 Structure description

In this work, the single crystal X-ray diffraction study revealed that compound **1** have asymmetric unit as illustrated in Fig.1. It is also observed that the structure of compound **1** is orthorhombic and it may be described in the following way. The structures of **1** is 3-D hybrid frameworks which are Pnma(62) space group. The dimensionality of its inorganic and organic connectivities are 1-D and 2-D, respectively. The 1-D inorganic chains contain of 9-coordinated europium polyhedra that participate their faces to form infinite zigzag chains along the [100] direction. To form the 2-D organic connectivity, europium chains are bridged by formate ligands along the [010] direction to form infinite 2-D layers, nearby layers are subsequently bridged by the oxalate ligands along the [001] direction to make a 3-D framework structure. 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 in Fig. 1.

3.2 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 Tb³⁺ transitions, respectively. The resonance energy levels of terbium ions are presented in Table.5 along with the various luminescence transitions.

Fig. 3) illustrates the photoluminescence spectra for compound **1**, there are four very strong characteristic emission bands for the Tb³⁺ ion in the visible region. The spectrum is dominated by the major sharp peak at 544 nm due to ⁵D₄→⁷F₅ transition which give strong green emission, as well as the other emission bands are: ⁵D₄→⁷F₆ at 486 nm and ⁵D₄→⁷F₄ at 583 nm and ⁵D₄→⁷F₃ at 620 nm, respectively. These transitions which are allowed by electric dipole (ED) and supersensitive to surrounding in the vicinity of Tb³⁺ ion, is very intense, emitting strong green luminescence [21].

Table 1. Crystallographic data of compound (1).

	1
<i>Formula sum</i>	<i>C₃H₁O₆Tb₁</i>
<i>Formula weight</i>	<i>291.96 g/mole</i>
<i>Crystal System</i>	<i>Orthorhombic</i>
<i>Space-Group</i>	<i>Pnma</i>
<i>Cell Parameters</i>	<i>a = 7.0138(3) Å, b = 10.6077(4) Å c = 6.66021(6) Å</i>
<i>α</i>	<i>90</i>

β	90
γ	90
$V(\text{\AA}^3)$	491.198
$D_c(\text{g cm}^{-3})$	3.948
Z	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)

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

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Tb1	0.00933(16)	0.00875(14)	0.00791(16)	-0.00050(9)	0.00000(10)	0.00000(13)
O1	0.0160(15)	0.0158(13)	0.0098(14)	0.0032(11)	-0.0012(11)	-0.0052(10)
O2	0.0164(15)	0.0294(18)	0.0162(17)	0.0005(14)	0.0012(13)	0.0090(15)

Atoms 1,2	$d_{1,2} [\text{\AA}]$	Atoms 1,2	$d_{1,2} [\text{\AA}]$
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)

Atoms 1, 2, 3	Angle 1, 2, 3 [°]	Atoms 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)		

Symmetry operators

- (i) $0.5+x, 0.5-y, 0.5-z$; (ii) $x, y, 0.5-z$; (iii) $0.5+x, 0.5-y, z$; (iv) $-x, -y, -z$;
(v) $-x, -y, 0.5+z$; (vi) $x, 1+y, z$; (vii) $-x, -y, -0.5+z$; (viii) $-0.5+x, 0.5-y, 0.5-z$;
(ix) $x, -1+y, z$.

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

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

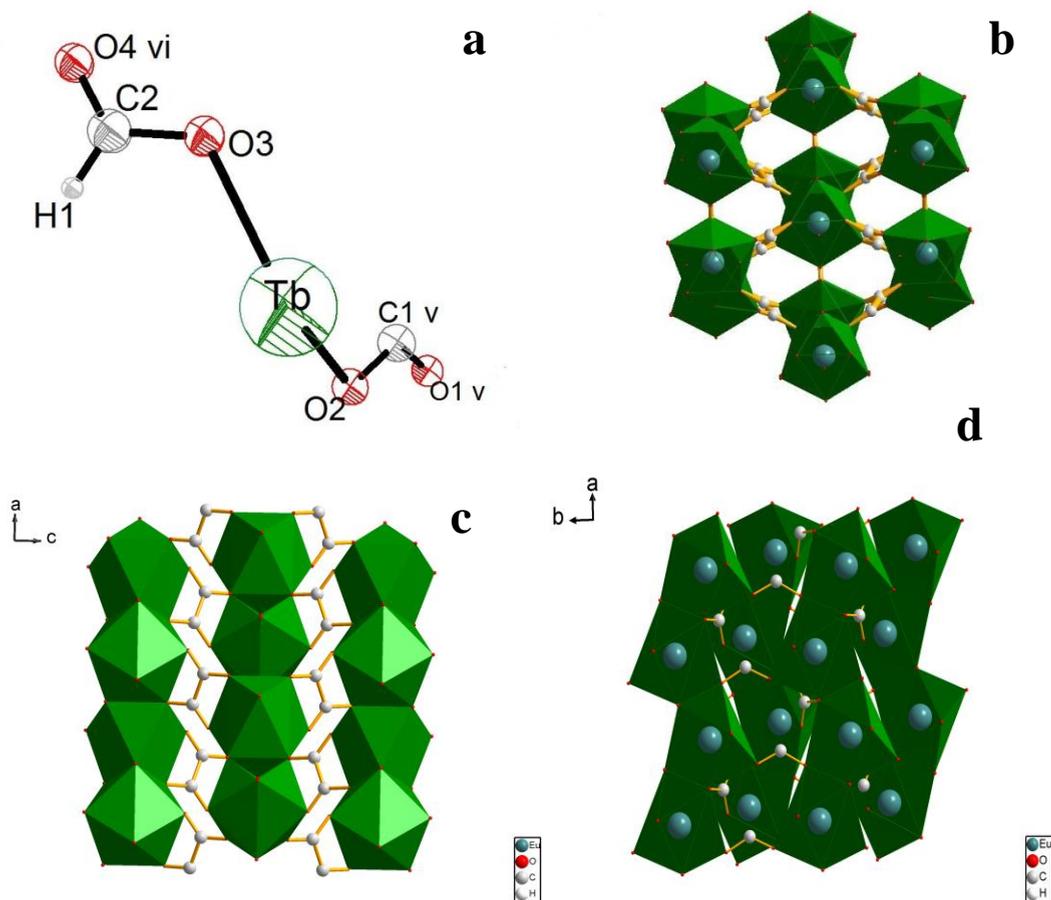


Fig. 1 Illustration of the crystal structure of the $Tb(C_2O_4)(HCOO)$ I hybrid framework with asymmetric unit. (a) Typical single crystal morphology (habit) and its low index face (b-d). Views perpendicular to the (100), (010), and (001) planes, respectively, hydrogen atoms have been deleted for clarity.

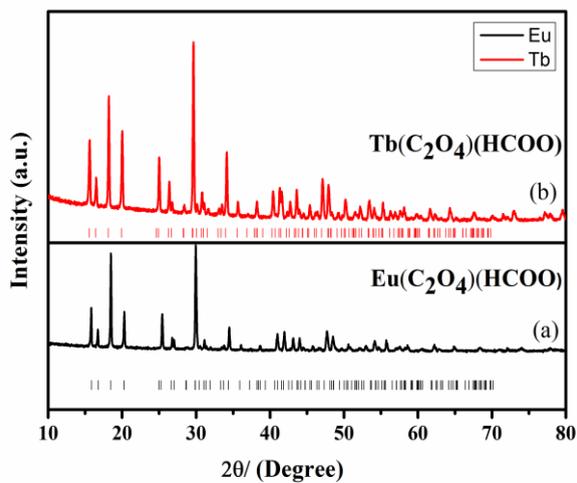


Fig. 2 The PXRD patterns of the as-synthesized $Tb(C_2O_4)(HCOO)$.

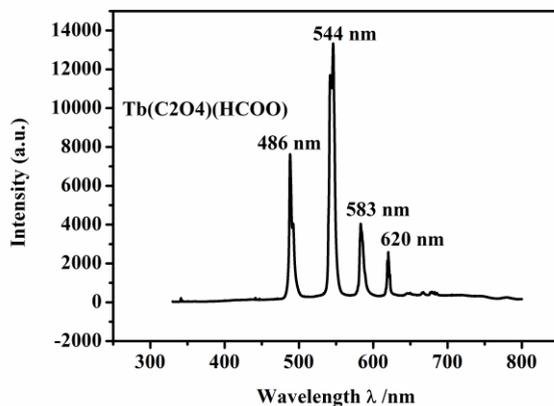


Fig. 3 PL spectra from compound of Tb compound.

4 Conclusion

In the presented work, 3-D hybrid framework **1** was successfully prepared through hydrothermal method and characterized by SCPXRD. Single crystal structure of compound **1** has asymmetric unit, and the spectrum of UV laser induced photoluminescence shows that compound **1** gave a strong green emission at 544 (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 light, field emission displays (FEDs).

References

- [1] Nada Abdul Hadi, Nadia Mohammed Jassim, Study of the structure and the luminescence properties of the Tb compound. *Journal of Engineering and Applied Sciences* 13(16):6787-6792, 2018.
- [2] (a) Du, M.; Jiang, X. J.; Zhao, X. J. *Inorg. Chem.* **2007**, 46, 3984–3985. (b) Lan., A. J.; Han, L.; Yuan, D. Q.; Jiang, F. L.; Hong, M. C. *Inorg. Chem. Commun.* **2007**, 10, 993–996. (c) Wang, X.-L.; Bi, Y.-F.; Lin, H.-Y.; Liu, G.-C. *Des.* **2007**, 7, 1086–1091. (d) Lu, Z.; Wen, L.; Ni, Z.; Li, Y.; Zhu, H.; Meng, Q. *Cryst. Growth Des.* **2007**, 7, 268–274.
- [3] (a) Sonnauer, A.; Nather, C.; Hoppe, H. A.; Senker, J.; Stock, N. *Inorg. Chem.* **2007**, 46, 9968–9974. (b) Gandara, F.; Garcia-Cortes, A.; Cascales, C.; Gomez-Lor, B.; Gutierrez-Puebla, E.; Iglesias, M.; Monge, A.; Snejko, N. *Inorg. Chem.* **2007**, 46, 3475–3484. (c) Serre, C.; Millange, F.; Thouvenot, C.; Gardant, F.; Férey, G. J. *Mater. Chem.* **2004**, 14, 1540–1543.
- [4] (a) de Lill, A.; Cahill, C. L. *Inorg. Chem.* **2007**, 46, 3960–3965. (b) McManus, G. J.; Perry, J. J.; Perry, M.; Wagner, B. D.; Zaworotko, M. J. *J. Am. Chem. Soc.* **2007**, 129, 9094–9101. (c) Chen, B. L.; Yang, Y.; Zapata, F.; Qian, G. D.; Luo, Y.S.; Zhang, J. H.; Lobkovsky, E. B. *Inorg. Chem.* **2006**, 45, 8882–8886. (d) Wagner, B. D.; McManus, G. J.; Moulton, B.; Zaworotko, M. J. *Chem. Commun.* **2002**, 2176–2177.
- [5] Hatanaka, M., Hirai, Y, T., Hasegawa, Y., Morokuma, K. *R. Chem. Sci.* **2016**, www.rsc.org/chemicalscience, DOI: 10.10309/c6sc03006h.
- [6] Rossin, A., Giambastiani, G., Peruzzini, M., Sessoli, R. *Inorg. Chem.* **2012**, 51, 6962-6968.
- [7] Latva, M., H. T. akalo, H., Mjukkala, V. M., Matachescu, C., Rodriguez-Ubis, C. J., Kankare, J. *Jour. Lumi.* **1997**, 75, 149-169.

- [8] Bunzil, J.C. G., Piguet, C. *Chem. Soc. Rev.* **2005**, 34, 1048-1077.
- [9] Cui, Y. G., Chen, L. B., Qian, D. G. *Coord. Chem. Rev.* **2014**, 273, 76-86.
- [10] Vicentini, G., Zinner, B. L., Zukerman-Schpector, J., Zinner, K. *Coord. Chem. Rev.* **2000**, 196, 353-382.
- [11] (a) Robin, Y. A., Fromm, M. K. *Coord. Chem. Rev.* **2006**, 250, 2127; (b) B. Chandler, D. B., Cramb, T. D., Shimizu, H. K. G., *J. Am. Chem. Soc.* **2006**, 128, 10403; (c) Pretsch, T., ,
- [12] Shang, M., Geng, D., Kang, X., Ypan, D., Zhang, Y., Lin, J. *Inorg. Chem.* **2012**, 51, 11106.
- [13] Sun, X., Zhang, H. W., Du, P. Y., Yan, G. Z., You, P. L., Yan, H. C. *Chem.-Eur. J.* **2007**, 13, 2320.
- [14] (a) Cheetham, A. K.; Rao, C. N. R.; Feller, R. K. *Chem. Commun.* **2006**, 4780-4795.
- [15] Rao, C. N. R., Natarajan, S., Vaidyanathan, R. *Angew. Chem., Int. Ed.* **2004**, 43, 1466-1496.
- [16] Romero, S., Mossoet, A.; Trombe, J. C. *J. Solid State Chem.* **1996**, 127, 256-266.
- [17] Latva, M., Takahlo, H., Mukkala, M. V., Matachescu, C., Rodrigues-Ubis, C. J., J. Kankare, J. J. *Lumin.* **1997**, 75, 149.
- [18] Freeman, J. J., Crosby, A. G. *J. Phys. Chem.* **1963**, 67, 2717.
- [19] Georges, J., Menmet, M. J. *Spectroscopic. Acta part A.* **1993**, 49, 397.
- [20] Carnell, W. T., Fields, P. R., Ramjnak, K. J. *Chem. Phys.* **1968**, 49, 4447.
- [21] Bünzli, C. J., Comby, S., Chauvin, S. A., Vandevyver, B. D. C. *J. Rare Earths*, **2007**, 25: 257-274.