

Cluster of Study of Terbium's Journey From Mine To 21st Century

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Abstract: An element found in the Ytterby mine, with 65 atomic number, nestled between its brother's gadolinium and dysprosium in the lanthanide series is a unique element.

Efficient magnetostriction, shown by alloy of terbium. Teflon-D an alloy of terbium, when magnetic field passed through has a unique character of, increasing and decreasing in its size. Is highly desired in the fields of nanotubes and materials. Herein, a new alloy with its unique property is anticipated to enhance the world of microfabrication research. Showing phosphorescence and its elaborate uses, would be used to stain biological cells, without any radioactive activity, would cut the exposure to radioactive material. Its property is in demand for low-energy lightbulbs and mercury lamps. Moreover, this research would offer an efficient self-understanding of this rare earth metal, and it's phenomenal work towards innovation in human welfare.

Index Terms: Magnetostriction, Nanotubes, Phosphorescence, radioactive material, Teflon- D, Ytterby mine

I. INTRODUCTION

CARL GUSTAF, found this element in a Swedish mine in 1787, Ytterby, although unable to isolate this element at that time, unaware the secrets this lanthanide element upholds, never found isolated in nature, it was earlier a sort of impurity (J. Feng and H. J. Zhang, 2013). Taking years to be isolated. the keen interest in terbium and its alloy is due to the unique size and property, result of the infamous lanthanide contraction. Terbium's structure, topology, periodic placement, spectral abilities like phosphorescence, absorption tendencies, unique magnetic property and spin gives results to its varied and multifield application and uses. In this work we'll study the isolation of terbium, its complexes and varied applications.

Terbium was isolated by chemist Moslander in 1843 in an earth called yttria, as yttria oxide, having +3 oxidation state Moore, E. G. Samuel, A. P. S. & Raymond K. N. Acc. Chem. Res. (2009), although it's not as its name suggests a rare earth metal is

quite ironic the abundance is 20 times that of silver so it's not that rare, its magnetic property is used in nanomaterials, due to its super paramagnetic form, therefore its intensely researched as some elements lose their magnetic and chemical properties with decrease in its size unlike terbium. For example, cuprite nanomaterial of terbium complexes is used in aircrafts or engine, for detection of damage in machine parts or as a replacement for those parts. Scientist come up with various technique to make much more efficient nickel terbium complex. In the present paper well learn more about its complexes and alloys.

Terbium complexes found in late 1900's with nickel, copper and ferrous not only show magnetic but electrical property as well (Bangarigadu-Sanasy, . R. Sankar, P. A. Dube, J. E. Greedan, and H. Kleinke, 2014). In nanomaterials the particle size is estimated through TEM analysis in 2006. Basically, reducing the particle size with doping of rare earth metal to it. Achieving stability by reducing assembling of doped particle at a certain vacancy (B. Webster, Ivanov, P., Russell, B. et al. (2019).

Terbium alloys, found in 2003 e.g., Teflon being an alloy of Dysprosium and Iron. Showing magnetostriction, in layman's term increasing and decreasing its size and shape (F. J. Darnell, 1963). By just adjusting the ratio of elements in the alloy we can extend the control its magnetostriction across varied temperature way beyond 0 degrees to 100 degrees (R. James Jennings, 1938). So, the question arises how is this achieved. It's used in small motors or small switches also used in strain gauges.

A phenomenon called as joule effect is a property of any ferromagnetic material. When in a material atom with similar magnetic orientation move axially in accordance to the electric or magnetic field provided to it, changes in its shape. Also, any mechanical done on its bulk would give an electrical response.

II. ISOLATION OF TERBIUM

Scandium, yttrium and lanthanides constitute a class of

elements generally known as “rare earth elements”. These elements and their alloys are used in high-tech technologies like smart phones and electric cars (Ogata et al. 2015). They have closely similar physical and chemical properties and are used in industries for the production of catalysts, pigments, cosmetics and medicines (Sereshti et al. 2012). They have excellent optical and magnetic properties and are therefore extensively used in lasers, lamps, super magnets and information storage devices (Zhao et al. 2016). The rare earth elements (REEs) including terbium (Tb) and others, are highly important for high-tech applications and industries. Several tons of these metals are required each year for commercial applications (Fryxell et al. 2011). The scraps and ores of lanthanides consist of high quantities of base metals particularly iron, and their selective separation and recovery pose a serious challenge to the researchers (Xie et al. 2014). For this purpose, the researchers have employed various techniques for their separations such as liquid-phase extraction (Tereshatov et al. 2015) based on ionic liquids (Dong et al. 2015), resins (Radhika et al. 2012), magnetic adsorbents (Basualto et al. 2015) and sorption-luminescence (Vasylechko et al. 2017) etc. Although solvent-extraction have been commonly employed for the extraction of lanthanides on large scale but recently, solid phase extraction has gained wide spread popularity (Radhika et al. 2012; Kumar et al. 2010; Huang et al. 2017) because of environment friendly nature, high efficiency and recovery of solid material. Amongst the solid phase materials, functionalized silica has received great attention for metals extraction (Bao et al. 2015), catalysis (García et al. 2018), dye adsorption.

III. SYNTHESIS OF LUMINESCENCE GUIDELINES

Molecular-type luminescent terbium containing hybrid materials were fabricated on the basis of modified 5-ethylpyridine-2,3-dicarboxylic acid by (3-aminopropyl)triethoxysilane (PDA-Si), emission centers and inorganic hosts. PDA-Si was demonstrated to show double functions which are utilized to coordinate to Tb³⁺ through carbonyl groups and covalently bonded with hosts by Si–O bonds after hydrolysis and polycondensation processes simultaneously. Ultraviolet absorption, phosphorescent spectra, and luminescent spectra were investigated to characterize the photophysical properties of the obtained hybrid material. It was shown that the triplet state energy of modified 5-ethylpyridine-2,3-dicarboxylic acid matches with the emissive energy level of Tb³⁺. More importantly, We unexpectedly observed some branches like morphology perhaps due to the formation tendency of 1-D chain crystal structure in original complex of 5-ethylpyridine-2, 3-dicarboxylic acid. The strong green fluorescence of terbium ions indicates that the molecular-designed hybrids have high photonic potential.

Six lanthanide coordination polymers of the formula [Ln(L₁)_{0.5}(H₂O)₂]₂·2H₂O [where Ln³⁺: Eu³⁺ (1), Tb³⁺ (2), and Gd³⁺(3)] and (H₂O)₄·0.5DMF·xH₂O [where Ln³⁺: Eu³⁺ (4), Tb³⁺

(5), and Gd³⁺(6)], based on -hexacarboxylate acid (H₆L₂), have been solvothermally synthesized and structurally characterized. Complexes 1–3 are 3D frameworks exhibiting 6-connected pcu alpha-Po primitive cubic network with topology (412.63), while complexes 4–6 show two-dimensional (2D) architectures showing simplified 3, 4-connected binodal net and topology. Detailed photophysical behaviors have been explored on Eu³⁺, Tb³⁺, and Gd³⁺ complexes. The calculated triplet state energies of H₆L₁ and H₆L₂ lie above the emissive levels of Eu³⁺.

IV. TERBIUM COMPLEXES

Tb³⁺ in an ideal range for sensitizing. (W. L. & Brill, A. Philips, 1964). Furthermore, it is demonstrated that the optimum energy gap between the triplet state of ligand H₆L₁ and the emissive level of Tb³⁺ ion makes the overall quantum yield of Tb³⁺ complex (2) larger than its corresponding Eu³⁺ complex (G, Wurzburg E., 1975). In addition, the coordinated water in the inner sphere has a significant negative influence on the overall quantum yield, especially for the Eu³⁺ complex (4) compared to the Tb³⁺ complex (5), due to the deactivation process caused by vibrational OH oscillators.

Two new complexes of Eu-bipyridine (Eu-AA and Eu-BB) were incorporated into sol-gel derived thin films based on zirconia oxide and organically modified sol-gel hybrid zirconia-silica-urethane ormocer (ZSUR) (Yang JH, Zhu GY, Wu, 1987).

The absorption and the emission intensities of the composites were compared to the intensity of the Eu oxide doped films and to the other complexes studied recently (Fotopoulou MA, Ioannou PC, 2002). The site symmetry of the Eu complexes and Eu oxide in used matrices were studied as well. The intensification of fluorescence, as compared to europium oxide, value was increased by a factor of 64 in amido-amino complex (Eu-AA), and of 2044 in fluorine complex (Eu-BB) as a result of efficient charge transfer from the combined ligand-europium state to europium high ligand levels. The lifetimes from the 5D₀ state of the complexes are measured and the results explained (Yang JH, Zhu GY, Wu, 1988).

The most common oxidation state of terbium is +3 (trivalent), such as TbCl₃. In the solid state, tetravalent terbium is also known, in compounds such as TbO₂ and TbF₄. (Ropp, R. C. J, 1964).

In solution, terbium typically forms trivalent species, but can be oxidized to the tetravalent state with ozone in highly basic aqueous conditions.

The coordination and organometallic chemistry of terbium is similar to other lanthanides. In aqueous conditions, terbium can be coordinated by nine water molecules, which are arranged in a tricapped trigonal prismatic molecular geometry. Complexes of terbium with lower coordination number are also known, typically with bulky ligands like bis(trimethyl-silylamide), which forms the three-coordinate Tb[N(SiMe₃)₂]₃ complex.

Most coordination and organometallic complexes contain

terbium in the trivalent oxidation state. Divalent (Tb^{2+}) complexes are also known, usually with bulky cyclopentadienyl-type ligands few coordination compounds containing terbium in its tetravalent state are also known.

A. Enhancement of Terbium(III)-Centered Luminescence

Terbium combines with nitrogen, carbon, sulfur, phosphorus, boron, selenium, silicon and arsenic at elevated temperatures, forming various binary compounds such as TbH_2 , TbH_3 , TbB_2 , Tb_2S_3 , $TbSe$, $TbTe$ and TbN . In those compounds, Tb mostly exhibits the oxidation states +3 and sometimes +2. Terbium(II) halogenides are obtained by annealing Tb(III) halogenides in presence of metallic Tb in tantalum containers. Terbium also forms sesquichloride Tb_2Cl_3 , which can be further reduced to $TbCl$ by annealing at 800 °C. This terbium(I) chloride forms platelets with layered graphite-like structure.

A series of luminescent phenoxo-bridged dinuclear Tb(III) complexes with tripodal ligands, 2,2'-[[2-(pyridinylmethyl)imino]di(methylene)]-bis(4-R-phenol), where R = CH_3 (LCH₃) (I), Cl (LCl) (II), CH_3O (LCH₃O) (III), $COOCH_3$ (LCOOCH₃) (IV), were prepared to probe the effect of para-substitution on the phenol ring of the ligand on the Tb(III) luminescence. For these Tb(III) complexes a complete suppression of the ligand-centered fluorescence is observed, which demonstrates an efficient ligand-to-metal energy transfer. Complex IV was found to be the one that shows the greater intensity of the emission at room temperature. The obtained quantum yields follow the trend $IV > II > I > III$.

The quantum yield for II and IV is approximately five times greater than those obtained for I and III, indicating that the LCl and LCOOCH₃ are better sensitizers of the Tb(III) ions. These results were rationalized in terms of the variation of the energy gap between the triplet level (T1) of the ligand and the emissive 5D₄ level of Tb(III), due to the electron-acceptor or electron-donor properties of the substituents. The τ_{av} values are in the millisecond range for all the studied complexes and resulted independent of temperature.

The Commission International d'Eclairage coordinates (CIE) for all in green color region, being insensitive to the variation of temperature. Moreover, the color purity (CP) is ca. 90% for all complexes, being ca. 100% for IV. Thus, the introduction of electron-acceptor substituents on the ligand permitted us to improve the luminescent properties of the Tb(III) complexes.

1) Organic Terbium Complex

Organic europium (III) and terbium (III) complexes (referred to as Eu1, Eu2, and Tb-L1, Tb-L2, respectively) have been synthesized that display bright emission and small bandwidth. Tb-L1 and Tb-L2 show lifetimes in the order of almost 1 ms at room temperature, good color purity, and high relative photoluminescence quantum yields. This makes them excellent probes for sensing temperature via measurement of

luminescence lifetime. Probes Eu1, Eu2, Tb-L1 and Tb-L2 were incorporated into various polymer matrices to give sensor films for use as temperature-sensitive paints (TSPs). Eu(III) complexes have the advantage of being effectively excited by purple light-emitting diodes with their peak wavelengths of 405 nm. All TSPs based on these europium and terbium probes display good sensitivities to temperature, in particular, TSP based on Tb-L1 and Tb-L2 can show temperature-lifetime sensitivities of $-13.8 \mu s$ per °C and $-9.2 \mu s$ per °C, respectively. Assuming a precision of $\pm 1 \mu s$ in the determination of lifetime, this will enable temperature to be determined with a precision of around ± 0.1 °C. This temperature dependence is the highest one reported so far for lanthanide complexes.

The luminescence of Tb^{3+} is important in a significant number of applications (Lis S. *Compd* 2002). Terbium is used in color phosphors in lighting applications such as trichromatic lighting and in color TV tubes. It also makes the green color on your Blackberry or other high definition screen (V. Uijtrent, Lida, S., 1926)

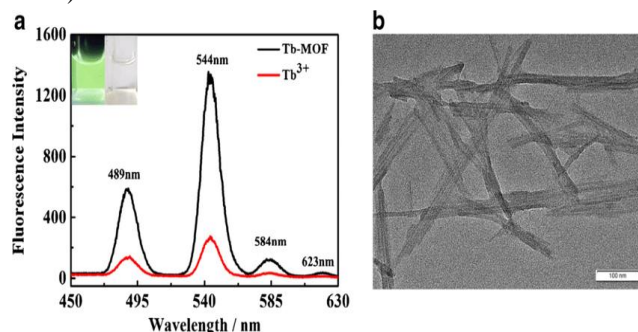


Fig. 1. Organic europium (III) and terbium (III) complexes, Fluorescence.

V. USES OF TERBIUM

Tb^{3+} ions can be used to check for the presence of microbes. Terbium chloride is applied to the test area, which is then illuminated with UV light. Within minutes, any live endospores present will glow green. Euro banknotes use rare earth chemistry to defeat counterfeiters. Shining UV light on a euro results in green fluorescence from terbium Tb^{3+} , red from europium Eu^{3+} , and blue from thulium Tm^{3+} .

A terbium-iron alloy is used to provide metallic films for magneto-optic recording of data.

Hybrid car engines have electric motors and all electric motors are based on magnets. These magnets need to retain their magnetism at high temperatures. Alloying neodymium with terbium and dysprosium produces such magnets. These magnets are also used in the electric motors of wind-turbines, where high temperatures are also generated.

Terfenol-D (a terbium, iron and dysprosium alloy) expands or contracts in the presence of a magnetic field (magnetostriction). It is used in a speaker called the 'SoundBug', which turns any flat surface into a speaker. The 'SoundBug' vibrates any material it is placed on, such as a table or desk, making it into a

speaker.

The binding properties of trivalent metal ions to polyelectrolytes were investigated through the use of terbium [Tb (III)] in fluorescence studies (BR, Jankowski JA, Leszczyszyn DJ, Wightman RM, Jorgensen JW. 1992). The fluorescence intensity and lifetimes of the lanthanide ions are directly dependent upon the number of water molecules bound to their inner coordination sphere (Volin P. 1994). The more efficiently a ligand coordinates to a lanthanide ion, the more water molecules are expelled and consequently, the greater the fluorescence intensity and lifetime. This effect was used to probe for differences in the complexation behavior of tactic polymers. Aqueous solutions of isotactic and syndiotactic poly(methacrylic acid) (PMA) were neutralized and complexed with Tb (III) ions. The fluorescence intensity of the 286 nm hypersensitive excitation band was monitored and the lifetimes were measured using several excitation wavelengths. It was found that the Tb (III) complex exhibited a six times greater fluorescence intensity than the syndiotactic PMA complex. Lifetime measurements gave the number of water molecules coordinated by Tb (III) in the isotactic complex to be 2.4 while 3.4 waters remained bound to the Tb (III) ion in the syndiotactic PMA complex. These results indicate that isotactic PMA has the greater binding affinity towards Tb (III) ions.

A spectrofluorimetric method was developed for the determination of catecholamines in serum samples based on terbium sensitized fluorescence. The proposed method is relatively simple, precise, rapid and more selective and sensitive than the many methods that have been used for the determination of catecholamines until now. The developed method was easily applied to the determination of catecholamines in serum samples with excellent reproducibility. This method does not require previous separation techniques due to the fact that there is no interference between catecholamines and the serum matrix.

As expected, complexation of catecholamines with Tb³⁺ ions depends strongly on the pH and occurs through dihydroxyphenyl group (Sinha, 1971). This result indicates that complexation involves two negatively charged oxygens available in a single ligand to form a chelate. Therefore, in order to form fluorescent chelates between catecholamines and Tb³⁺ ions, it is necessary to work in alkaline media because the optimum pH for the complex formation seems related to the dissociation of the phenol group. However, the aqueous solutions of catecholamines, decompose rapidly in alkaline medium (pH=10.5, after 15 min.). Therefore, in order to prevent their oxidation in alkaline medium, that is necessary for the complex formation, sodium sulphite was used. The results indicated that in the presence of Na₂SO₃, the complexes were stable for 24 h and their fluorescence intensity were enhanced.

It is well known that water molecules strongly quench terbium

sensitized fluorescence (Arnaud N, Georges J, 2001). The presence of synergistic agents, that complete the coordination sphere of lanthanide ion by displacing water molecules from ligand field, and the various surfactants, which protects these chelates from non-radiative processes, have been usually used to improve the fluorescence of these systems in solutions .

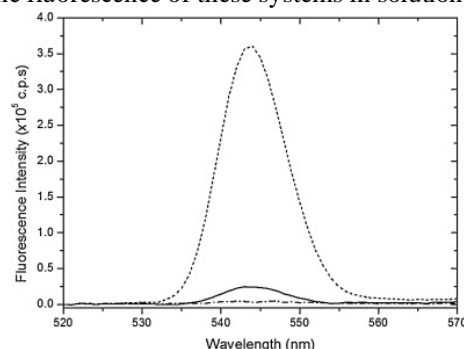


Fig 2 . Terbium organic complex , Fluorescence

CONCLUSION

Its future use in nano materials, nanotubes would make our future. Its past use in lamps, and today's use in CRTs and TV sets exported terbium to all of us. Historically used in lamps, as terbium salts and complexes. Located in lanthanide series it's still unexplored. Till 2018 its phosphorescence was called wrongly fluorescence. In this paper we saw the journey of a unique element from dark Swedish quarry to being isolated 100 years by mistake. Under the trials and tests of the mankind's innovation with it.

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