

Chemistry of the Elements



Europium

Maxime Bardiau, Jonas Wolfsberger, Leoni Klingelhöfer

How does Europium keep your money safe?

Why were so many people watching Europium daily?

Why is Europium not like the other Lanthanoids?



About the Element and Reactivity

Special applications



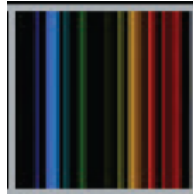
63 151.9
Eu
Europium
[Xe] 4f⁷ 6s
Lanthanides



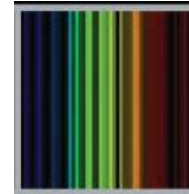
Discovery, Abundancy, Production

Compounds, Use and Properties

Discovery



^{62}Sm



^{64}Gd



1885 Crook

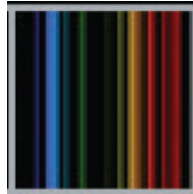


1892 De Boisbaudran

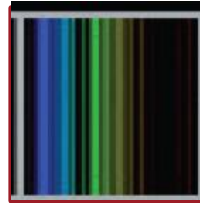


1896 Demarçay

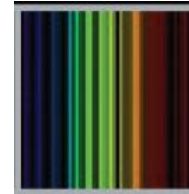
Discovery



^{62}Sm



^{63}Eu



^{64}Gd



1885 Crook



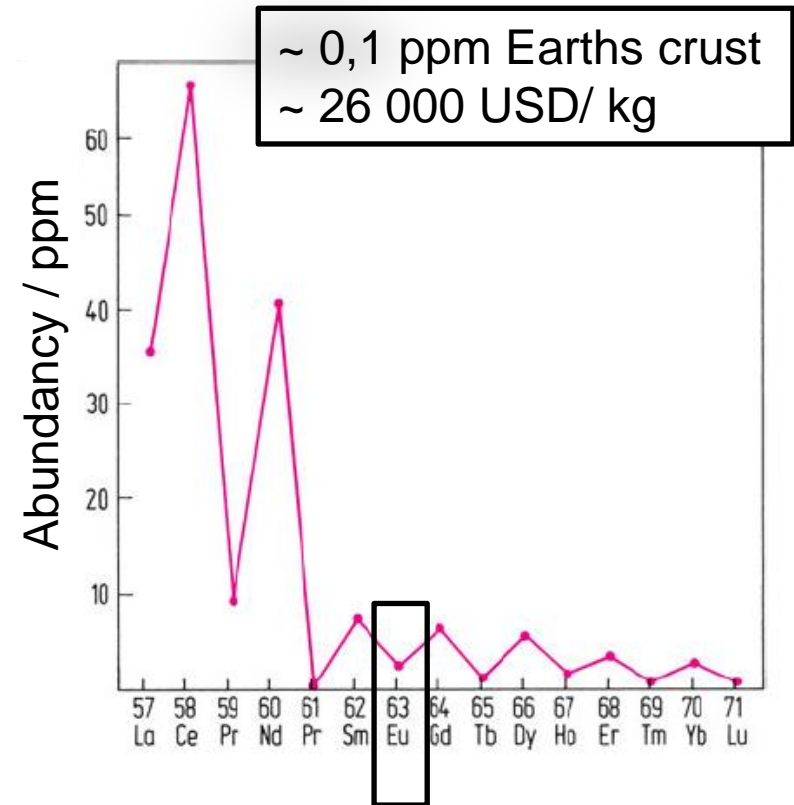
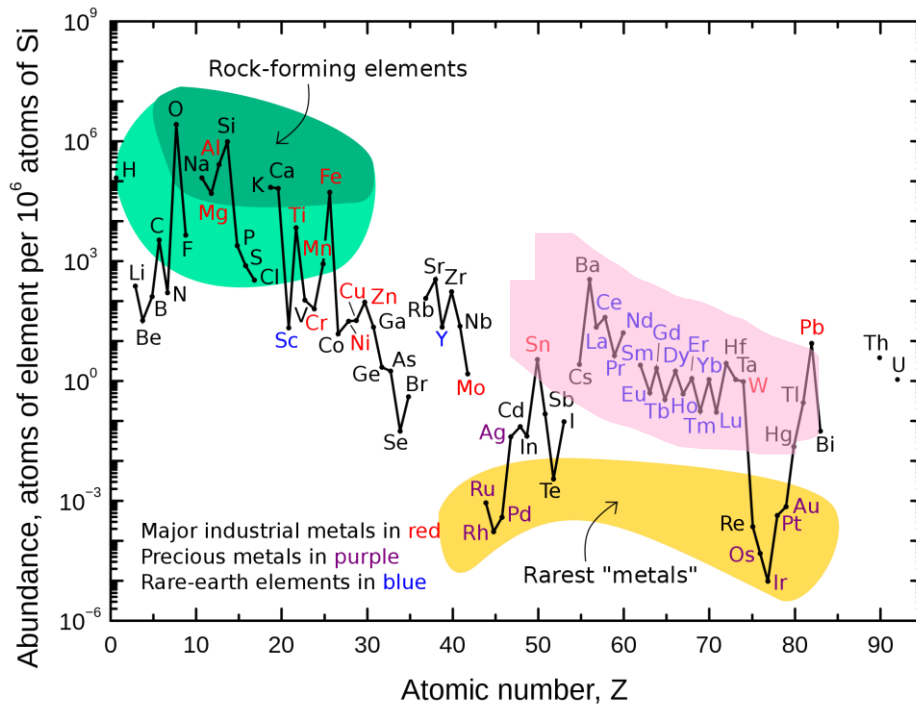
1892 De Boisbaudran



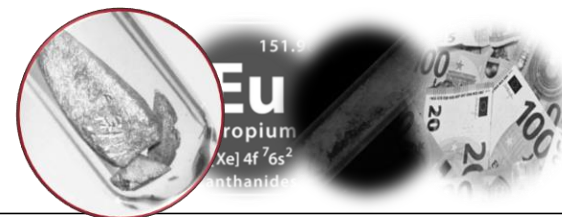
1896 Demarçay



Abundance



Abundance



Rare earth metals production and reserves

2018 PRODUCTION
Tonnes

RESERVES
Million tonnes



Source: USGS

*Data not available

© AFP

Production



Monazite



Bastnasite

- Solvent extraction
- Ion exchange & Complex building
- Precipitation (with bases)



https://upload.wikimedia.org/wikipedia/commons/a/a2/Bastnaesit_Burundi.jpg

<https://upload.wikimedia.org/wikipedia/commons/6/63/Monazite-%28Ce%29-Quartz-273341.jpg?20100427085329>

https://th.bing.com/th/id/R.6d24271a395e8eb078a784cad9352c0f?rik=cNQzBsQYj0jytg&riu=http%3a%2f%2fclearlyexplained.com%2f_Media%2feuopium_med_hr.jpg&ehk=3XRGFCnhVLF1uBYhrEf20hSrq4Z8IEtNXmPd3ISU6CI%3d&risl=&pid=ImgRaw&r=0

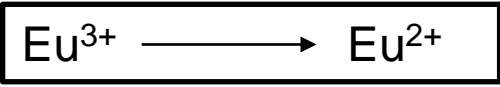
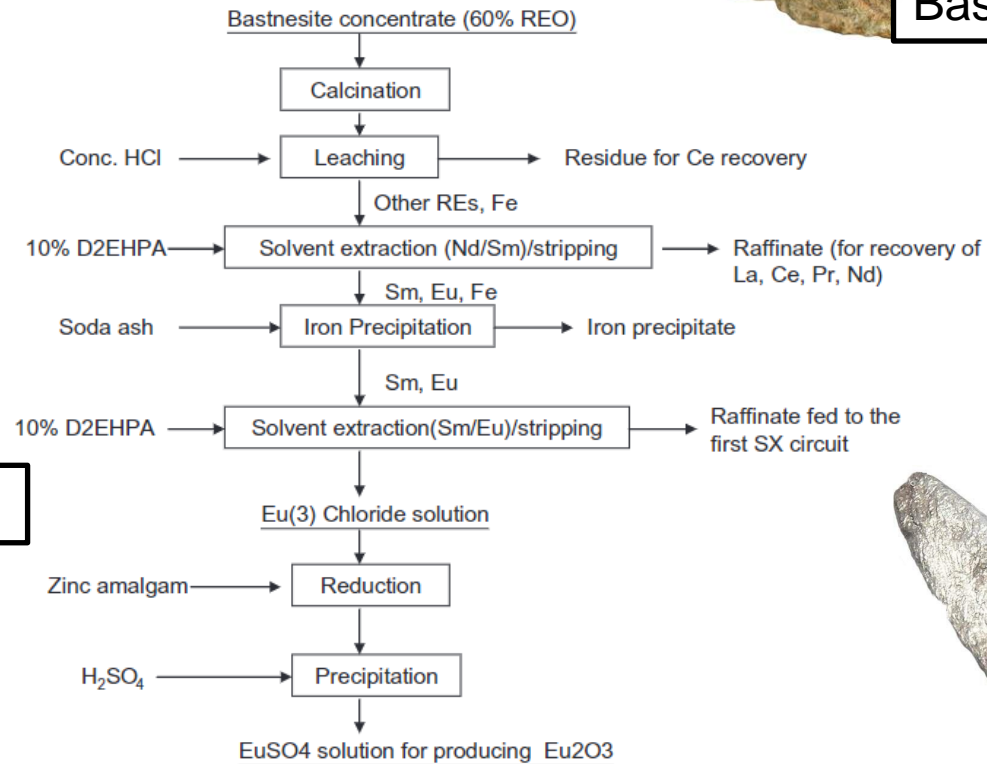
Production



- Solvent extraction

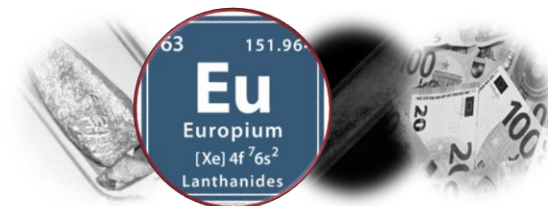


Bastnasite



<https://reader.elsevier.com/reader/sd/pii/S0892687513003452?token=0DA5B583EF7CD556DE3E924EA946C6C7470E0C9BDFB201B6B383F0FCB25C0DD840F7CE342959C4AA3EC51211A374B3E7&originRegion=eu-west-1&originCreation=20221005160835>

Position in the periodic table



63 151.964

Eu

Europium

[Xe] 4f⁷ 6s²

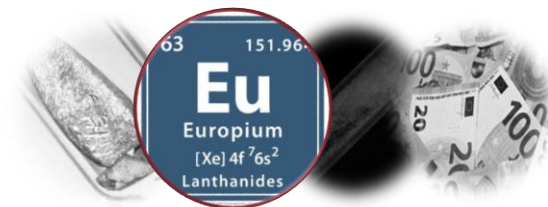
Lanthanides

ChemistryLearner.com

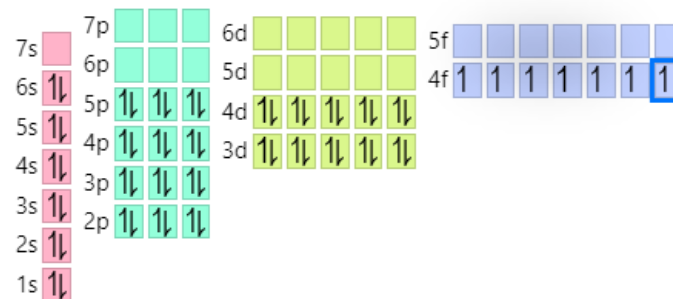
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18		
1	H Hydrogen 1.008																	He Helium 4.0026		
2	Li Lithium 6.94	Be Beryllium 9.0122											B Boron 10.81	C Carbon 12.011	N Nitrogen 14.007	O Oxygen 15.999	F Fluorine 18.998	Ne Neon 20.180		
3	Na Sodium 22.990	Mg Magnesium 24.305											Al Aluminum 26.982	Si Silicon 28.085	P Phosphorus 30.974	S Sulfur 32.06	Cl Chlorine 35.45	Ar Argon 39.948		
4	K Potassium 39.098	Ca Calcium 40.078	Sc Scandium 44.956	Ti Titanium 47.867	V Vanadium 50.942	Cr Chromium 51.996	Mn Manganese 54.938	Fe Iron 55.845	Co Cobalt 58.933	Ni Nickel 58.693	Cu Copper 63.546	Zn Zinc 65.38	Ga Gallium 69.723	Ge Germanium 72.630	As Arsenic 74.922	Se Selenium 78.971	Br Bromine 79.904	Kr Krypton 83.798		
5	Rb Rubidium 85.468	Sr Strontium 87.62	Y Yttrium 88.906	Zr Zirconium 91.224	Nb Niobium 92.906	Mo Molybdenum 95.95	Tc Technetium (98)	Ru Ruthenium 101.07	Rh Rhodium 102.91	Pd Palladium 106.42	Ag Silver 107.87	Cd Cadmium 112.41	In Indium 114.82	Sn Tin 118.71	Sb Antimony 121.76	Te Tellurium 127.60	I Iodine 126.90	Xe Xenon 131.29		
6	Cs Caesium 132.91	Ba Barium 137.33	57-71		Hf Hafnium 178.49	Ta Tantalum 180.95	W Tungsten 183.84	Re Rhenium 186.21	Os Osmium 190.23	Ir Iridium 192.22	Pt Platinum 195.08	Au Gold 196.97	Hg Mercury 200.59	Tl Thallium 204.38	Pb Lead 207.2	Bi Bismuth 208.98	Po Polonium (209)	At Astatine (210)	Rn Radon (222)	
7	Fr Francium (223)	Ra Radium (226)	89-103		Rf Rutherfordium (267)	Db Dubnium (268)	Sg Seaborgium (269)	Bh Bohrium (270)	Hs Hassium (277)	Mt Meitnerium (276)	Ds Darmstadtium (281)	Rg Roentgenium (282)	Cn Copernicium (285)	Nh Nihonium (286)	Fl Flerovium (289)	Mc Moscovium (290)	Lv Livermorium (293)	Ts Tennessine (294)	Og Oganesson (294)	
																			For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.	
	La Lanthanum 138.91	Ce Cerium 140.12	Pr Praseodymium 140.91	Nd Neodymium 144.24	Pm Promethium (145)	Sm Samarium 150.36	Eu Europium 151.96	Gd Gadolinium 157.25	Tb Terbium 158.93	Dy Dysprosium 162.50	Ho Holmium 164.93	Er Erbium 167.26	Tm Thulium 168.93	Yb Ytterbium 173.05	Lu Lutetium 174.97					
	Ac Actinium (227)	Th Thorium 232.04	Pa Protactinium 231.04	U Uranium 238.03	Np Neptunium (237)	Pu Plutonium (244)	Am Americium (243)	Cm Curium (247)	Bk Berkelium (247)	Cf Californium (251)	Es Einsteinium (252)	Fm Fermium (257)	Md Mendelevium (258)	No Nobelium (259)	Lr Lawrencium (260)					

Ptable® is a registered trademark of Michael Dayah (support@pstable.com). For a fully-interactive edition in 50 languages with property trend visualization, 3-D orbitals, isotopes, compound mixing, lesson plans, posters, wallet cards, and installable apps, visit Ptable.com.
 Meek, J., Cooper, T., Bergantini, M., et al. (2016). Atomic weights of the elements 2013 (IUPAC Technical Report). Pure and Applied Chemistry, 88(1), 265-291.

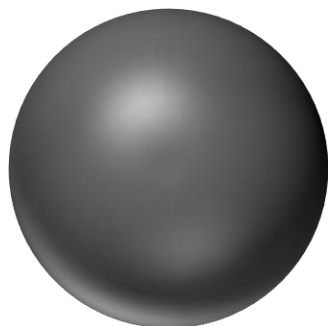
Chemical features



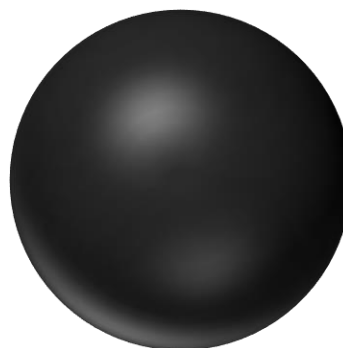
- $[\text{Xe}]4f^76s^2$
- Oxidation states: +2 and +3



<https://ptable.com/?lang=en#Electrons>



187pm



200pm

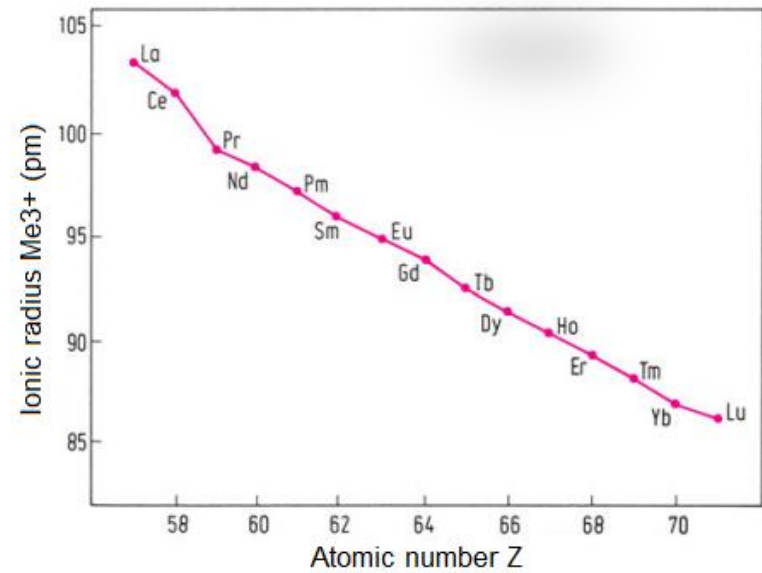
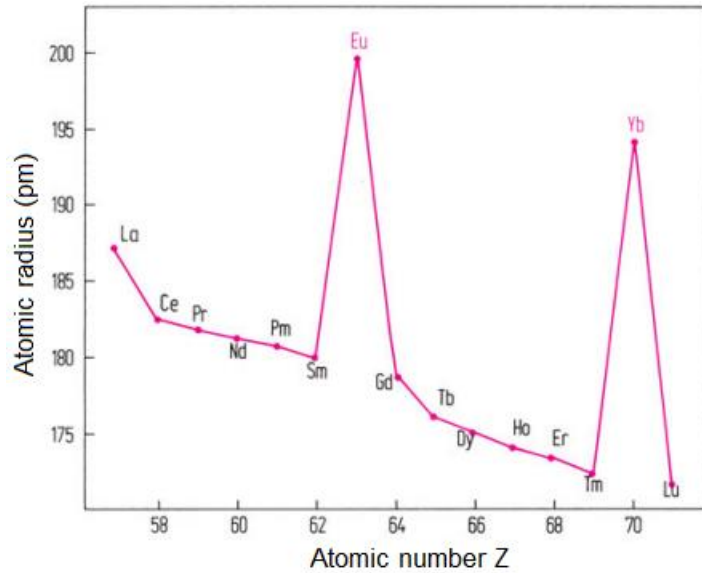
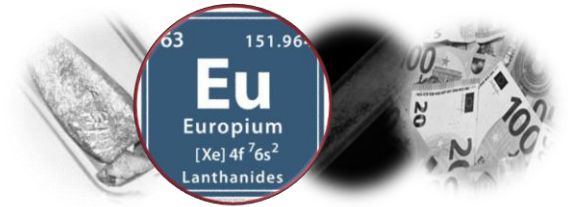


28pm

Riedel, E. & Janiak, C. *Anorganische Chemie. Anorganische Chemie* (De Gruyter, 2011).
doi:10.1515/9783110225679.

https://www.webelements.com/helium/atom_sizes.html

Radius



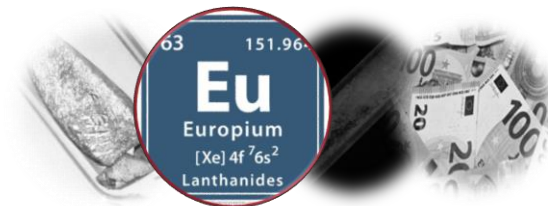
Riedel, E. & Janiak, C. *Anorganische Chemie. Anorganische Chemie* (De Gruyter, 2011). doi:[10.1515/9783110225679](https://doi.org/10.1515/9783110225679).

Usually 3 electrons in the conduction band \longrightarrow Eu and Yb have only 2

\longrightarrow Larger radii

Chemistry of the Elements, N.N. Greenwood & A. Earnshaw, Pergamon Press.

Reactivity



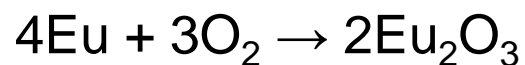
- Reactivity depends on the size



Eu: most reactive rare-earth

Chemistry of the Elements, N.N. Greenwood & A. Earnshaw, Pergamon Press.

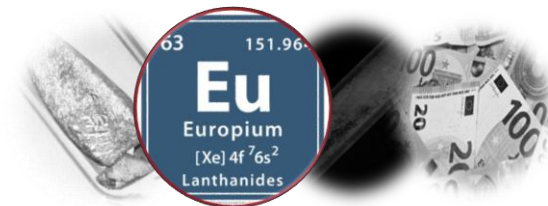
- Oxidation:



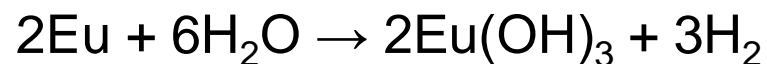
<http://www.epi-materials.com/europium-oxide-eu2o3/>

Europium - an overview | ScienceDirect Topics. <https://www.sciencedirect.com/topics/materials-science/europium>.

Reactivity



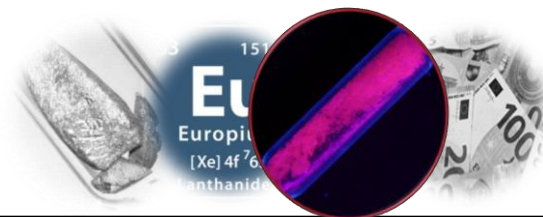
- Reaction with water:



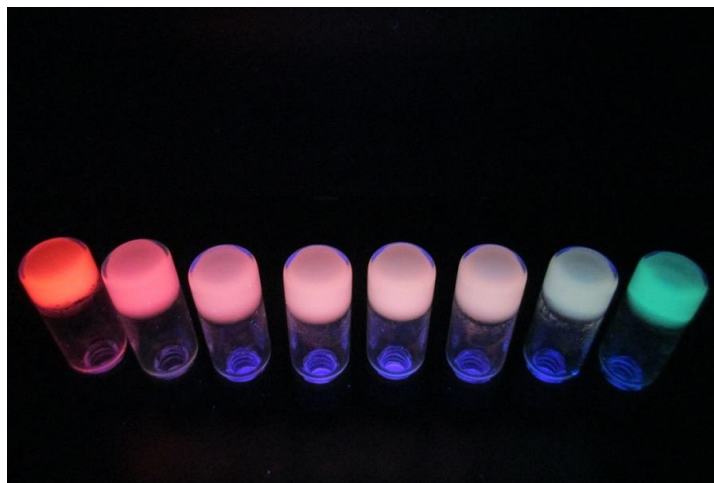
- Dilution in Sulfuric acid:



Compounds of Europium

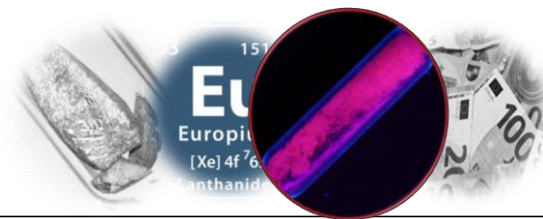


- Chalcogenides (oxygen, sulfur, selenium and tellurium)
- Halides (fluorine, chlorine, bromine and iodide)
- Compounds with sulfate and nitrate are also known
- Eu-based complexes



Massachusetts Institute of Technology. <https://news.mit.edu/> (accessed 2022-10-05)

Europium chalcogenides



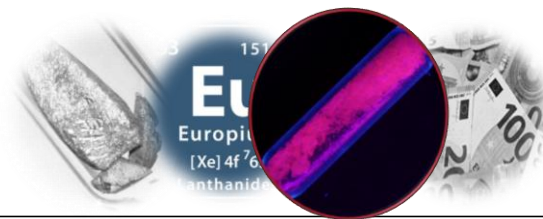
- EuO europium(II)oxide
- Eu_2O_3 europium(III)oxide
- Mixed-valenced europium(II,III)oxide
- EuS europium(II)sulfide
- EuSe europium(II)selenide
- EuTe europium(II)telluride



Reddit. <https://www.reddit.com> (accessed 2022-10-04)

Pavlov, V.V. Linear and Nonlinear Magneto-optical Phenomena in Epitaxial Films of Europium Chalcogenides EuX ($X = \text{O}, \text{Se}, \text{Te}$). *Phys. Solid State* **61**, 408–413 (2019). <https://doi.org/10.1134/S1063783419030247>

Properties of europium chalcogenides



- unique electronic, magnetic, optical, and magneto-optical properties
- EuS, EuSe and EuTe are black solids and stabilize the lower oxidation state
- EuO and EuS are ferromagnets
- EuSe is metamagnetic
- EuTe is antiferromagnetic

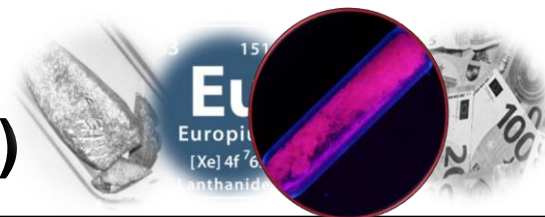


Boncher, William, et al. Europium chalcogenide magnetic semiconductor nanostructures. *Coordination Chemistry Reviews* **289**, 279-288 (2015).

Pavlov, V.V. Linear and Nonlinear Magneto-optical Phenomena in Epitaxial Films of Europium Chalcogenides EuX (X = O, Se, Te). *Phys. Solid State* **61**, 408–413 (2019). <https://doi.org/10.1134/S1063783419030247>

Europium halides

(oxidation states +II and +III)



EuF_2 and EuF_3 europiumfluoride

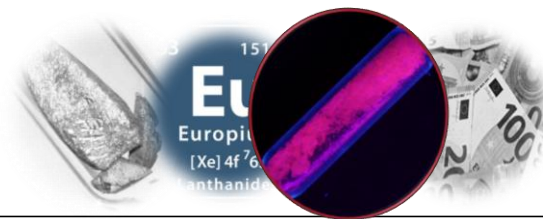
EuCl_2 and EuCl_3 europiumchloride

EuBr_2 and EuBr_3 europiumbromide

EuI_2 and EuI_3 europiumiodide

Holleman, A. F.; Wiberg, E. N. Anorganische Chemie; De Gruyter, 2017

Properties of europium halides

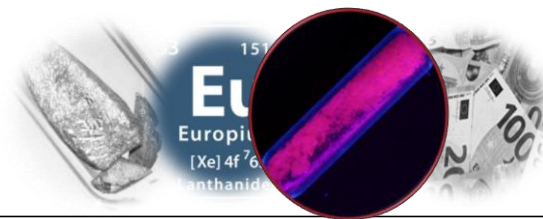


- Most of them are hygroscopic
- Europium fluorides are used as phosphor activators
- Europium(III) chloride is used as a starting material for the preparation of other europium salts
- Europium bromide is a ferromagnetic material
- Europium iodides are used as a heat and light stabilizer for nylon fabrics

Chemical Book. <https://m.chemicalbook.com/> (accessed 2022-10-05)

American Elements. <https://www.americanelements.com/> (accessed 2022-10-05)

Europium(III)sulfate and europium(III)nitrate



- $\text{Eu}_2(\text{SO}_4)_3$ europium(III) sulfate



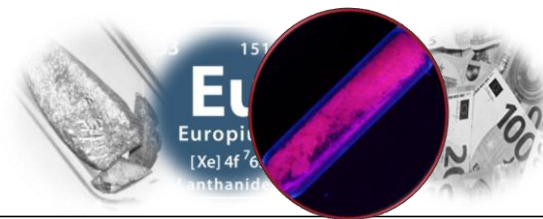
Wikipedia. <https://en.wikipedia.org/> (accessed 2022-10-06)

- $\text{Eu}(\text{NO}_3)_3$ europium(III) nitrate

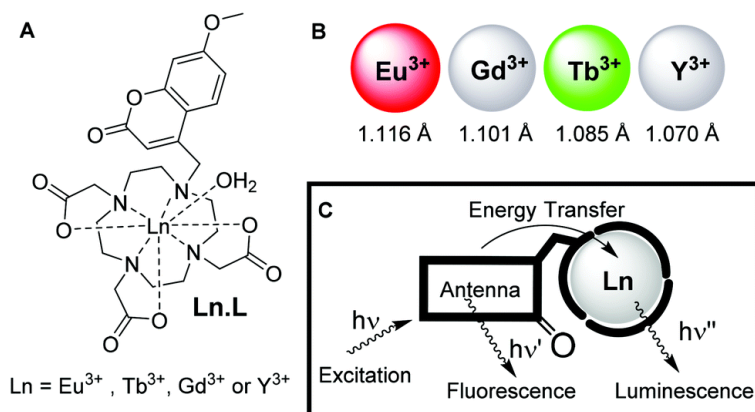


Wikipedia. <https://en.wikipedia.org/> (accessed 2022-10-06)

Europium based complexes



- Inorganic and organic compounds as ligands
- Wide range of application due to luminescence
- Luminescence occurs from antenna effect



Junker, A. K. R.; Hill, L. R.; Thompson, A. K.; et al. Shining light on the antenna chromophore in lanthanide based dyes. *Dalton Transactions*. 2018, **47**, 4794-4803 DOI: <https://doi.org/10.1039/C7DT04788F>

Ipha, B.; Ballardini, R.; Balzani, V.; et al. Antenna Effect In Luminescent Lanthanide Cryptates: A Photophysical Study. *Photochem. Photobiol.* 1990, **52**, 299–306.

Have you ever held a euro note under UV light?



- Euro notes appear green, red and orange under UV light
- Security ink for anti-counterfeiting documents e.g bank notes, passports or cards



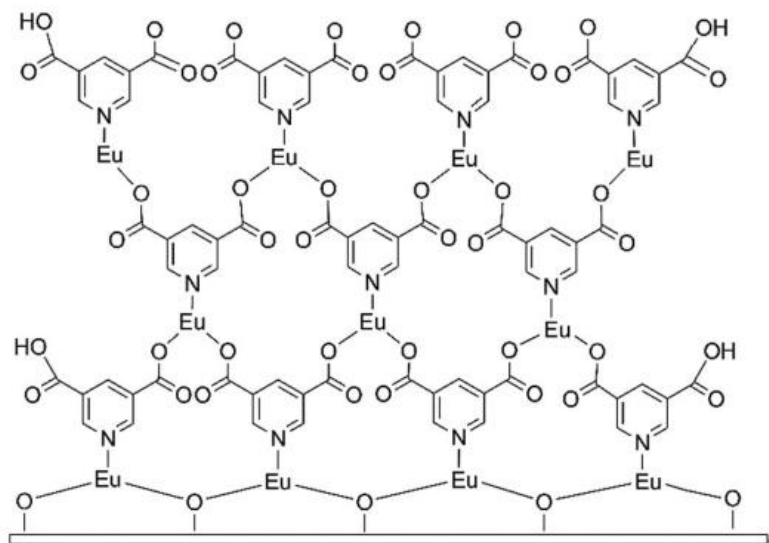
Banco de Portugal. <https://www.bportugal.pt/> (accessed 2022-10-04)

Flexible inorganic–organic thin film phosphors by ALD/MLD



Motivation:

- Good luminescence of europium-based materials



Precursors:

- Eu(2,2,6,6- tetramethyl-3,5- heptanedione)₃
- 3,5-pyridine-dicarboxylic acid

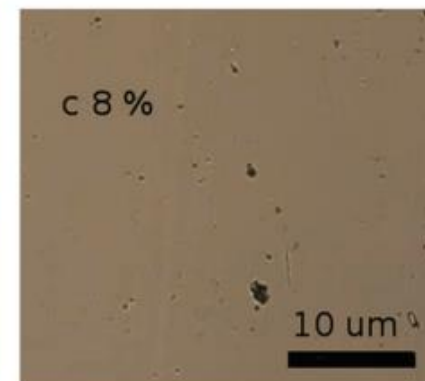
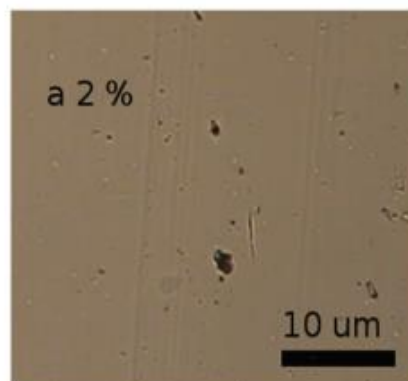
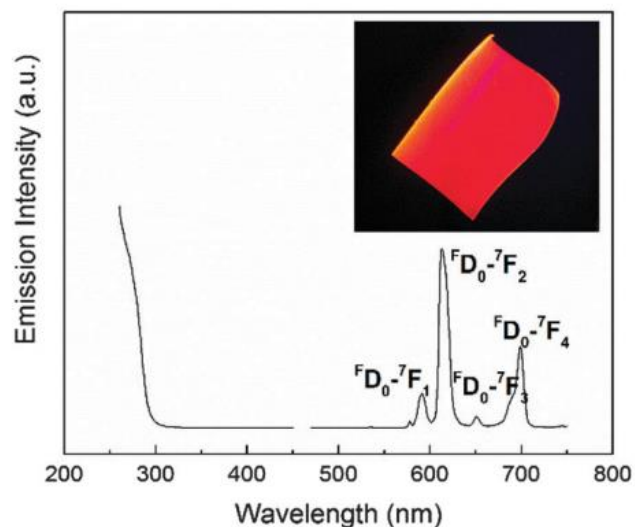
Giedraityte, Z., Sundberg, P. & Karppinen, M. Flexible inorganic–organic thin film phosphors by ALD/MLD. *J. Mater. Chem. C* 3, 12316–12321 (2015).

Flexible inorganic–organic thin film phosphors by ALD/MLD



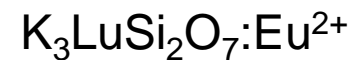
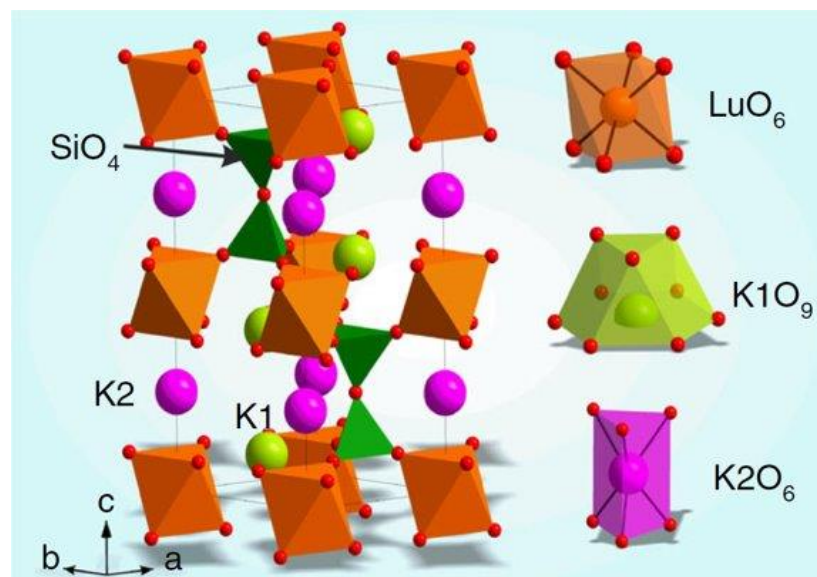
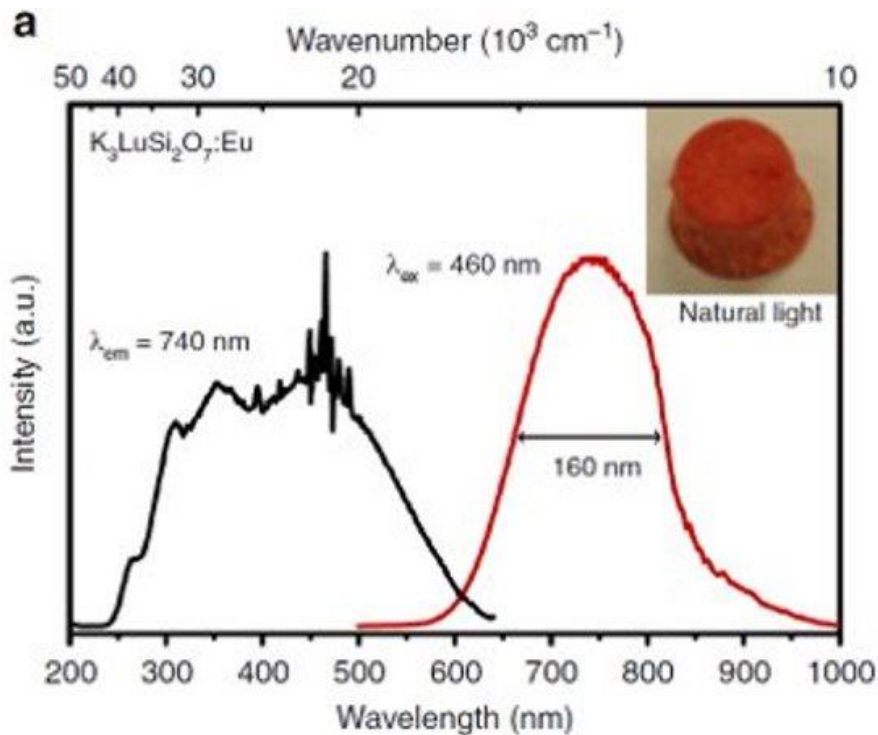
Properties:

- Highly uniform and stable
- High luminescence intensities.
- Highly flexible



Giedraityte, Z., Sundberg, P. & Karppinen, M. Flexible inorganic–organic thin film phosphors by ALD/MLD. *J. Mater. Chem. C* 3, 12316–12321 (2015).

Eu²⁺ doped near-infrared phosphor for LEDs



Eu²⁺ doped near-infrared phosphor for LEDs

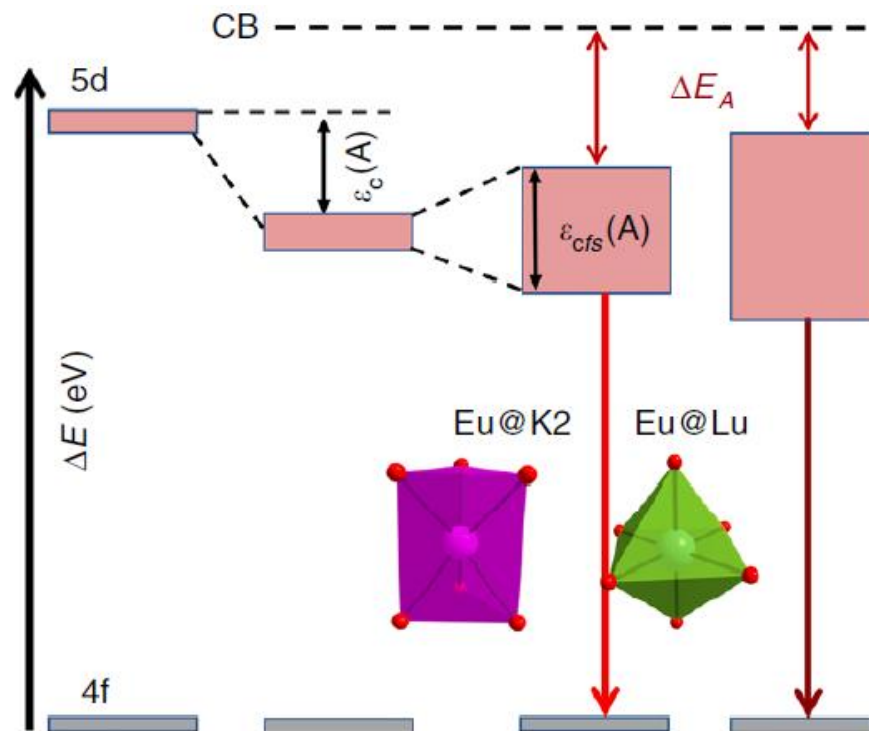


Natural light

Light off

NIR light on

Eu²⁺ doped near-infrared phosphor for LEDs





That's all Folks!