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Lanthanide (Ln^{57-71})

Properties

The Lanthanides or lanthanoid series of chemical elements comprises the 15 metals with atomic numbers 57 through 71, from lanthanum through lutetium.

The Lanthanides share many similar characteristics. These characteristics include the following:

- Similarity in physical properties throughout the series
- Lanthanides exist overwhelmingly in their +3 oxidation sate, although particularly stable 4f configurations can also give +4 (Ce, Pr, Nd, Tb) or +2 (Nd, Eu, Tm, Yb) ions.
- Adoption of coordination numbers greater than 6 (usually 8-9) in compounds
- Tendency to decreasing coordination number across the series
- A preference for more electronegative elements (such as O or F) binding
- Very small crystal-field effects
- Little dependence on ligands
- Ionic complexes undergo rapid ligand-exchange

The Lanthanides have a silvery shine when freshly cut. However, they can tarnish quickly in air, especially Ce, La and Eu. These elements react with water slowly in cold, though that reaction can happen quickly when heated. This is due to their electropositive nature. The Lanthanides have the following reactions:

- oxidize rapidly in moist air
- dissolve quickly in acids
- reaction with oxygen is slow at room temperature, but they can ignite around 150-200 °C
- react with halogens upon heating
- upon heating, react with S, H, C and N

Electrode potentials for lantanide metal deposition are very negative, ranging from -2V to -3V, more specifically, electrode potentials are the following: La in respect to La^{3+} (La/ La^{3+}) is – 2.379V; Ce/Ce^{3+} - 2.336V; Pr/Pr^{3+} - 2.353V and Pr/Pr^{2+} -2.0V; Nd/Nd^{3+} -2.323V and Nd/Nd^{2+} -2.1V; Sm/Sm^{+2} -2.68V and Sm/Sm^{3+} -2.304V; Eu/Eu^{+2} -2.812V and Eu/Eu^{+3} -2.331V; Gd/Gd^{3+} - 2.279V; Tb/Tb^{3+} -2.28V; Dy/Dy^{3+} -2.295V and Dy/Dy^{2+} -2.2V; Ho/Ho^{3+} - 2.33V and Ho/Ho^{2+} -2.1V; Er/Er^{2+} -2V; Tm/Tm^{2+} -2.4V and Tm/Tm^{3+} - 2.319V; Yb/Yb^{2+} -2.76V and Yb/Yb^{3+} -2.19V; Lu/Lu^{3+} - 2.28V.

One property of the Lanthanides that affect how they will react with other elements is called the basicity. Basicity is a measure of the ease at which an atom will lose electrons. For the Lanthanides, the basicity series is the following:

$$La^{3+} > Ce^{3+} > Pr^{3+} > Nd^{3+} > Pm^{3+} > Sm^{3+} > Eu^{3+} > Gd^{3+} > Tb^{3+} > Dy^{3+} > Ho^{3+} > Er^{3+} > Tm^{3+} > Yb^{3+} > Lu^{3+}$$

In other words, the basicity decreases as the atomic number increases. Basicity differences are shown in the solubility of the salts and the formation of the complex species.

Another property of the Lanthanides is their magnetic characteristics. The major magnetic properties of any chemical species are a result of the fact that each moving electron is a micromagnet. The species are either diamagnetic, meaning they have no unpaired electrons, or paramagnetic, meaning that they do have some unpaired electrons. The diamagnetic ions are: La^{3+}, Lu^{3+}, Yb^{2+} and Ce^{4+}. The rest of the elements are paramagnetic.

The Lanthanides have similarities in their electron configuration, which explains most of the physical similarities. These elements are different from the main group elements in the fact that they have electrons in the f orbital. After Lanthanum, the energy of the 4f sub-shell falls below that of the 5d sub-shell. This means that the electron start to fill the 4f sub-shell before the 5d sub-shell.

Table 1. Physical properties of the Lanthanides.

Chemical element	Atomic number	Atomic Weight	Density (g/cm^3)	Melting Point (^oC)	Resistivity ($\mu\Omega$ cm)	Brinell Hardness, MPa	Abundance in crust (ppm)
Lanthanum (La)	57	138.9	6.162	920	61.5	350-400	39
Cerium (Ce)	58	140.1	6.770	795	82.8	186-412	66
Praseodymium (Pr)	59	140.9	6.77	935	68	250-640	9.1
Neodymium (Nd)	60	144.2	7.01	1024	64	265-700	41.5
Promethium (Pm)	61	147	7.26	1142	75	NA	None
Samarium (Sm)	62	150.4	7.52	1072	94	440-600	7
Europium (Eu)	63	152	5.244	826	90	160-190	2
Gadolinium (Gd)	64	157.3	7.9	1312	131	485-903	6.2
Terbium (Tb)	65	158.9	8.23	1356	115	675-1200	1.2
Dysprosium (Dy)	66	162.5	8.54	1407	57	500-1050	5.2
Holmium (Ho)	67	164.9	8.79	1461	87	500-1250	1.4
Erbium (Er)	68	167.3	9.066	1529	87	600-1070	2.8
Thulium (Tm)	69	168.9	9.32	1545	79	470-900	0.5
Ytterbium (Yb)	70	173	6.9	824	29	340-440	3
Lutetium (Lu)	71	175	9.841	1652	79	890-1300	0.5

Plating Solutions

Lanthanide can be electrodeposited from aqueous solutions [1-3], organic electrolytes [4,5,10], molten salt baths [6,7,8], and ionic liquids [9,10].

Molten salts and organic electrolytes are widely used to electrodeposit the lantanide and their alloys. For example, lutetium and lutetium-magnesium electroplating can be performed in molten LiCl-KCl and LiCl-KCl-$MgCl_2$ bath in the temperature range of 400 – 550 ^oC [8, 9]. The anhydrous solvent DMSO (Dimethyl Sulfoxide) can be used to electrodeposit neodymium at temperature of 30 ^oC [10].

Iron-group metals induce co-deposition of lanthanides in aqueous solutions, molten salts and organic electrolytes. For example, iron induces codeposition of terbium in citrate and tartrate electrolytes [1]. Samarium deposition was obtained at 1.15V in the presence of cobalt and samarium was preferentially deposited over cobalt with samarium content in the deposit reaching as high as 79 wt.% from the molten bath [6]. Acceleration of samarium deposition rate caused by cobalt can be also achieved from organic electrolytes.

Pure Erbium and Terbium as well as Silicon–Erbium (Si/Er) and silicon–terbium (Si/Tb) thin films can be electrodeposited from 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([Py]TFSI) ionic liquid [11] . Lantanum electrodeposition in ambient atmosphere can be obtained in 1-octyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide ionic liquid [12].

Applications

About 85% of the lanthanide production is consumed as catalysts and in the production of glasses [13]. The devices lanthanide elements are used in include superconductors, samarium-cobalt and neodymium-iron-boron high-flux rare-earth magnets, holmium pole pieces of the strongest static magnets (Ho has the highest magnetic permeability of any element), magnesium alloys, electronic polishers (cerium oxide for CMP of silica), refining catalysts and hybrid car components (primarily batteries and magnets).

Lanthanide ions are used as the active ions in luminescent materials for optoelectronics applications, most notably the Nd:YAG and Er:YAG lasers. Most lanthanides are widely used in lasers, and as (co-)dopants in doped-fiber optical amplifiers; for example, in Er-doped fiber amplifiers, which are used as repeaters in the terrestrial and submarine fiber-optic transmission links that carry internet traffic.

Phosphors with lanthanide dopants are also widely used in cathode ray tube technology. Yttrium iron garnet (YIG) spheres can act as tunable microwave resonators. Lanthanide oxides are mixed with tungsten to improve their high temperature properties. Many defense-related products also use lanthanide elements such as night vision goggles, rangefinders and radars.

References:

1. J. Gong and E.J Podlaha. *Electrochemical and Solid State Letters* (**3**), 422-425, 2000.
2. M.Schwartz, N.V. Myung, and K. Nobe. *J. Electrochem. Soc.* (**151**), C468-C477, 2004
3. C.D. Lokhande, R.D. Madhale, and S.H. Pawar. *Metal Finishing* (**86**), 23-25, 1988.
4. P. Liu, Q.Q. Yang, Y.S. Yang, and Y.X. Tong. *Journal of Rare Earths* **17**, 151-154, 1999.
5. P. Liu, Q.Q. Yang, Y.X. Tong, and Y.S. Yang. *Electrochimica Acta* **45**, 2147-2152, 2000.
6. P.Liu, Y.P. Du, Q.Q. Yang, Y.X. Tong, and G.A. Hope. *J. Electrochem. Soc* **153**, C57-C62, 2006.
7. Y.X. Tong et al. *Journal of Rare Earths* **23**, 72-74, 2005.
8. T. Jiang et al. *Journal of Alloys and Compounds* **658**, 198-209, 2016.
9. E. Barrado et al. *Journal of Electroanalytical Chemistry* **617**(1), 85-100, 2008.
10. E. Bourbos et al. *Metals* **8**, 803, 2018.
11. S. Thomas, J. Mallet, H. Rinnert, and M. Molinari. *RSC Adv*. **8**, 3789-3797, 2018.
12. S. Legeai et al. *Electrochemistry Communications* **10**(11), 1661-1664, 2008.
13. I. McGill. "Rare Earth Elements" in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, 2005.

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