

= Samarium =

Samarium is a chemical element with symbol Sm and atomic number 62 . It is a moderately hard silvery metal that readily oxidizes in air . Being a typical member of the lanthanide series , samarium usually assumes the oxidation state + 3 . Compounds of samarium (II) are also known , most notably the monoxide SmO , monochalcogenides SmS , SmSe and SmTe , as well as samarium (II) iodide . The last compound is a common reducing agent in chemical synthesis . Samarium has no significant biological role and is only slightly toxic .

Samarium was discovered in 1879 by the French chemist Paul Émile Lecoq de Boisbaudran and named after the mineral samarskite from which it was isolated . The mineral itself was earlier named after a Russian mine official , Colonel Vasili Samarsky @-@ Bykhovets , who thereby became the first person to have a chemical element named after him , albeit indirectly . Although classified as a rare earth element , samarium is the 40th most abundant element in the Earth 's crust and is more common than such metals as tin . Samarium occurs with concentration up to 2 @. @ 8 % in several minerals including cerite , gadolinite , samarskite , monazite and bastnäsite , the last two being the most common commercial sources of the element . These minerals are mostly found in China , the United States , Brazil , India , Sri Lanka and Australia ; China is by far the world leader in samarium mining and production .

The major commercial application of samarium is in samarium @-@ cobalt magnets , which have permanent magnetization second only to neodymium magnets ; however , samarium compounds can withstand significantly higher temperatures , above 700 ° C (1 @, @ 292 ° F) , without losing their magnetic properties , due to the alloy 's higher Curie point . The radioactive isotope samarium @-@ 153 is the major component of the drug samarium (153Sm) lexidronam (Quadramet) , which kills cancer cells in the treatment of lung cancer , prostate cancer , breast cancer and osteosarcoma . Another isotope , samarium @-@ 149 , is a strong neutron absorber and is therefore added to the control rods of nuclear reactors . It is also formed as a decay product during the reactor operation and is one of the important factors considered in the reactor design and operation . Other applications of samarium include catalysis of chemical reactions , radioactive dating and an X @-@ ray laser .

= = Physical properties = =

Samarium is a rare earth metal having the hardness and density similar to those of zinc . With the boiling point of 1794 ° C , samarium is the third most volatile lanthanide after ytterbium and europium ; this property facilitates separation of samarium from the mineral ore . At ambient conditions , samarium normally assumes a rhombohedral structure ($\sqrt{3}$ form) . Upon heating to 731 ° C , its crystal symmetry changes into hexagonally close @-@ packed (hcp) , however the transition temperature depends on the metal purity . Further heating to 922 ° C transforms the metal into a body @-@ centered cubic (bcc) phase . Heating to 300 ° C combined with compression to 40 kbar results in a double @-@ hexagonally close @-@ packed structure (dhcp) . Applying higher pressure of the order of hundreds or thousands of kilobars induces a series of phase transformations , in particular with a tetragonal phase appearing at about 900 kbar . In one study , the dhcp phase could be produced without compression , using a nonequilibrium annealing regime with a rapid temperature change between about 400 and 700 ° C , confirming the transient character of this samarium phase . Also , thin films of samarium obtained by vapor deposition may contain the hcp or dhcp phases at ambient conditions .

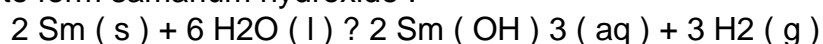
Samarium (and its sesquioxide) are paramagnetic at room temperature . Their corresponding effective magnetic moments , below 2 μ B , are the 3rd lowest among the lanthanides (and their oxides) after lanthanum and lutetium . The metal transforms to an antiferromagnetic state upon cooling to 14 @. @ 8 K. Individual samarium atoms can be isolated by encapsulating them into fullerene molecules . They can also be doped between the C60 molecules in the fullerene solid , rendering it superconductive at temperatures below 8 K. Samarium doping of iron @-@ based superconductors ? the most recent class of high @-@ temperature superconductors ? allows to

enhance their transition temperature to 56 K , which is the highest value achieved so far in this series .

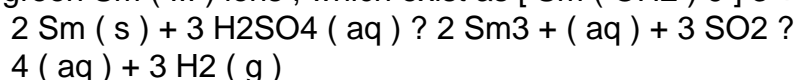
= = Chemical properties = =

Freshly prepared samarium has a silvery luster . In air , it slowly oxidizes at room temperature and spontaneously ignites at 150 ° C. Even when stored under mineral oil , samarium gradually oxidizes and develops a grayish @-@ yellow powder of the oxide @-@ hydroxide mixture at the surface . The metallic appearance of a sample can be preserved by sealing it under an inert gas such as argon .

Samarium is quite electropositive and reacts slowly with cold water and quite quickly with hot water to form samarium hydroxide :



Samarium dissolves readily in dilute sulfuric acid to form solutions containing the yellow to pale green Sm (III) ions , which exist as [Sm (OH₂)₉]³⁺ complexes :



Samarium is one of the few lanthanides that exhibit the oxidation state + 2 . The Sm²⁺ ions are blood @-@ red in aqueous solution .

= = Compounds = =

= = = Oxides = = =

The most stable oxide of samarium is the sesquioxide Sm₂O₃ . As many other samarium compounds , it exists in several crystalline phases . The trigonal form is obtained by slow cooling from the melt . The melting point of Sm₂O₃ is rather high (2345 ° C) and therefore melting is usually achieved not by direct heating , but with induction heating , through a radio @-@ frequency coil . The Sm₂O₃ crystals of monoclinic symmetry can be grown by the flame fusion method (Verneuil process) from the Sm₂O₃ powder , that yields cylindrical boules up to several centimeters long and about one centimeter in diameter . The boules are transparent when pure and defect @-@ free and are orange otherwise . Heating the metastable trigonal Sm₂O₃ to 1900 ° C converts it to the more stable monoclinic phase . Cubic Sm₂O₃ has also been described .

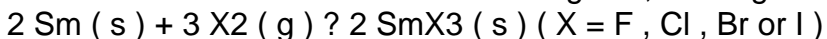
Samarium is one of the few lanthanides that form a monoxide , SmO . This lustrous golden @-@ yellow compound was obtained by reducing Sm₂O₃ with samarium metal at elevated temperature (1000 ° C) and pressure above 50 kbar ; lowering the pressure resulted in an incomplete reaction . SmO has the cubic rock @-@ salt lattice structure .

= = = Chalcogenides = = =

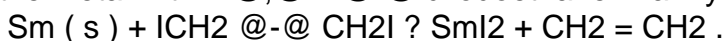
Samarium forms trivalent sulfide , selenide and telluride . Divalent chalcogenides SmS , SmSe and SmTe with cubic rock @-@ salt crystal structure are also known . They are remarkable by converting from semiconducting to metallic state at room temperature upon application of pressure . Whereas the transition is continuous and occurs at about 20 ? 30 kbar in SmSe and SmTe , it is abrupt in SmS and requires only 6 @.@ 5 kbar . This effect results in spectacular color change in SmS from black to golden yellow when its crystals or films are scratched or polished . The transition does not change lattice symmetry , but there is a sharp decrease (~ 15 %) in the crystal volume . It shows hysteresis , that is when the pressure is released , SmS returns to the semiconducting state at much lower pressure of about 0 @.@ 4 kbar .

= = = Halides = = =

Samarium metal reacts with all the halogens , forming trihalides :



Their further reduction with samarium , lithium or sodium metals at elevated temperatures (about 700 ? 900 ° C) yields dihalides . The diiodide can also be prepared by heating SmI₃ , or by reacting the metal with 1 @, @ 2 @-@ diiodoethane in anhydrous tetrahydrofuran at room temperature :



In addition to dihalides , the reduction also produces numerous non @-@ stoichiometric samarium halides with a well @-@ defined crystal structure , such as Sm₃F₇ , Sm₁₄F₃₃ , Sm₂₇F₆₄ , Sm₁₁Br₂₄ , Sm₅Br₁₁ and Sm₆Br₁₃ .

As reflected in the table above , samarium halides change their crystal structures when one type of halide atoms is substituted for another , which is an uncommon behavior for most elements (e.g. actinides) . Many halides have two major crystal phases for one composition , one being significantly more stable and another being metastable . The latter is formed upon compression or heating , followed by quenching to ambient conditions . For example , compressing the usual monoclinic samarium diiodide and releasing the pressure results in a PbCl₂ @-@ type orthorhombic structure (density 5 @. @ 90 g / cm³) , and similar treatment results in a new phase of samarium triiodide (density 5 @. @ 97 g / cm³) .

= = = Borides = = =

Sintering powders of samarium oxide and boron , in vacuum , yields a powder containing several samarium boride phases , and their volume ratio can be controlled through the mixing proportion . The powder can be converted into larger crystals of a certain samarium boride using arc melting or zone melting techniques , relying on the different melting / crystallization temperature of SmB₆ (2580 ° C) , SmB₄ (about 2300 ° C) and SmB₆₆ (2150 ° C) . All these materials are hard , brittle , dark @-@ gray solids with the hardness increasing with the boron content . Samarium diboride is too volatile to be produced with these methods and requires high pressure (about 65 kbar) and low temperatures between 1140 and 1240 ° C to stabilize its growth . Increasing the temperature results in the preferential formations of SmB₆ .

= = = Samarium hexaboride = = =

Samarium hexaboride is a typical intermediate @-@ valence compound where samarium is present both as Sm²⁺ and Sm³⁺ ions at the ratio 3 : 7 . It belongs to a class of Kondo insulators , that is at high temperatures (above 50 K) , its properties are typical of a Kondo metal , with metallic electrical conductivity characterized by strong electron scattering , whereas at low temperatures , it behaves as a non @-@ magnetic insulator with a narrow band gap of about 4 ? 14 meV . The cooling @-@ induced metal @-@ insulator transition in SmB₆ is accompanied by a sharp increase in the thermal conductivity , peaking at about 15 K. The reason for this increase is that electrons themselves do not contribute to the thermal conductivity at low temperatures , which is dominated by phonons , but the decrease in electron concentration reduced the rate of electron @-@ phonon scattering .

New research seems to show that it may be a topological insulator .

= = = Other inorganic compounds = = =

Samarium carbides are prepared by melting a graphite @-@ metal mixture in an inert atmosphere . After the synthesis , they are unstable in air and are studied also under inert atmosphere . Samarium monophosphide SmP is a semiconductor with the bandgap of 1 @. @ 10 eV , the same as in silicon , and high electrical conductivity of n @-@ type . It can be prepared by annealing at 1100 ° C an evacuated quartz ampoule containing mixed powders of phosphorus and samarium . Phosphorus is highly volatile at high temperatures and may explode , thus the heating rate has to be kept well below 1 ° C / min . Similar procedure is adopted for the monarsenide SmAs , but the synthesis temperature is higher at 1800 ° C.

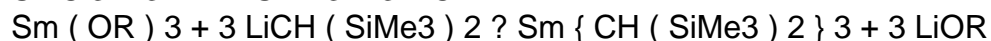
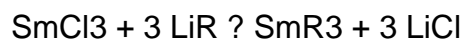
Numerous crystalline binary compounds are known for samarium and one of the group 4, 5 or 6 element X, where X is Si, Ge, Sn, Pb, Sb or Te, and metallic alloys of samarium form another large group. They are all prepared by annealing mixed powders of the corresponding elements. Many of the resulting compounds are non stoichiometric and have nominal compositions Sm_aX_b , where the b/a ratio varies between 0.5 and 3.

== Organometallic compounds ==

Samarium forms a cyclopentadienide $\text{Sm}(\text{C}_5\text{H}_5)_3$ and its chloroderivatives $\text{Sm}(\text{C}_5\text{H}_5)_2\text{Cl}$ and $\text{Sm}(\text{C}_5\text{H}_5)\text{Cl}_2$. They are prepared by reacting samarium trichloride with NaC_5H_5 in tetrahydrofuran. Contrary to cyclopentadienides of most other lanthanides, in $\text{Sm}(\text{C}_5\text{H}_5)_3$ some C_5H_5 rings bridge each other by forming ring vertexes or edges toward another neighboring samarium atom, thereby creating polymeric chains. The chloroderivative $\text{Sm}(\text{C}_5\text{H}_5)_2\text{Cl}$ has a dimer structure, which is more accurately expressed as $(\text{C}_5\text{H}_5)_2\text{Sm}(\mu\text{Cl})_2(\text{C}_5\text{H}_5)_2$. There, the chlorine bridges can be replaced, for instance, by iodine, hydrogen or nitrogen atoms or by CN groups.

The $(\text{C}_5\text{H}_5)^-$ ion in samarium cyclopentadienides can be replaced by the indenide $(\text{C}_9\text{H}_7)^-$ or cyclooctatetraenide $(\text{C}_8\text{H}_8)^{2-}$ ring, resulting in $\text{Sm}(\text{C}_9\text{H}_7)_3$ or $\text{KSm}(\text{C}_8\text{H}_8)_2$. The latter compound has a similar structure to that of uranocene. There is also a cyclopentadienide of divalent samarium, $\text{Sm}(\text{C}_5\text{H}_5)_2$, a solid that sublimates at about 85°C . Contrary to ferrocene, the C_5H_5 rings in $\text{Sm}(\text{C}_5\text{H}_5)_2$ are not parallel but are tilted by 40° .

Alkyls and aryls of samarium are obtained through a metathesis reaction in tetrahydrofuran or ether:



Here R is a hydrocarbon group and Me stands for methyl.

== Isotopes ==