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## Physical Properties Of Rare Earth Elements

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### ABSTRACT

The article studies the physical properties of rare earth metals, pays special attention to their unique properties, studies the main aspects of the application of rare earth metals in industry.

Also, the structure and stability of various forms of sesquioxides of rare earth elements, in particular, europium, as well as the effect of the method of oxide preparation on its structure and properties are considered. The analysis of the ongoing phase transformations of rare earth metals is made. The article emphasizes the use of correct choices to achieve a large technical and economic effect when using rare earth metals in industry.

The article is intended for teachers working in the field of physics and chemistry, as well as for students of the specialty "physics and chemistry".

### KEYWORDS

REM, recrystallization, alloy, oxide, phase transformations, technical and economic effect.

### INTRODUCTION

Rare earth elements - elements - metals of a silvery-white color, some with a yellowish tint (Pr, Nd). They are plastic and electrically conductive, easy to machine. Many properties of simple substances and compounds change

symmetrically in the La-Eu and Gd-Yb series. The properties that reflect the transition from a bound state to a free state and vice versa are especially sharply different. For example, in the transition from a metallic state to a vapor state,

the vapor pressure of the metals is the measure. At 25 °C, the vapor pressures of REE differ by more than 40 orders of magnitude, and at 1000 °C, by about 10 orders of magnitude (the minimum pressure is typical for La, Gd, and Lu, the maximum - for Eu and Yb). This is due to the large difference in energy required for the transition of a 4 d electron to

the 5d level. On the other hand, there are properties that remain approximately constant for all REEs. As a result of lanthanide contraction on going from La to Lu, the ionic radii of REEs and their atomic radii (except for Eu and Yb) smoothly decrease (Fig. 1, 2), and the density of simple substances increases [31].

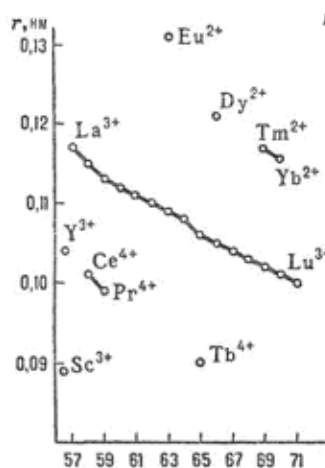


Fig. 1

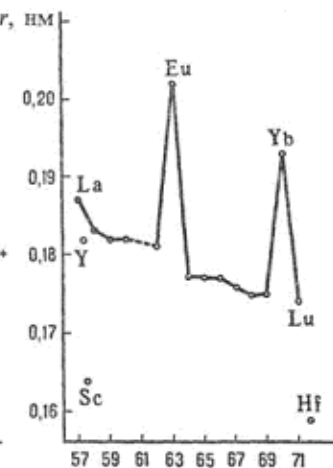


Fig. 2

**The dependence of the atomic radii of rare earth elements on their atomic number**

## MATERIALS AND METHODS

In recent decades, the demand for rare earth metals has a steady upward trend; over the past 50 years, the market volume has increased from 5 to 125 thousand tons per year. This is due to the use of rare earth metals in rapidly developing areas of industry related to the production of hybrid vehicles, defense technology, computer and television equipment, lasers, superconductors and other high technology products (production of magnets - 22%; high-quality optics and glass - 15%; catalysts - 18%; construction materials - 19%; other - 26%). The properties of rare earth metals find their application, first of all, in the

military-industrial and aerospace sectors of the economy and, therefore, are strategic metals.

In the monograph of Serebryannikov [9] there is an indication that light rare-earth metals ignite when heated in an oxygen atmosphere: as a result of combustion, oxides are formed. Without heating, the metal surface in a dry air atmosphere remains for a rather long time, in humid air it quickly becomes covered with an oxide layer.

Somewhat more detailed data can be found in the works of Kremers [10] and Love [11]. The rate of atmospheric corrosion was determined

by Love on metal specimens cut in the form of plates at temperatures of 35 and 950. The experiments were carried out at different relative humidity. Tests at temperatures of 200, 400, and 600 ° were carried out in a tubular furnace through which a weak air flow was blown.

At atmospheric oxidation of rare earth metals, hydrated oxides with a large volume increase are formed. This leads to destruction of the protective oxide film and exposure of the metal surface. The coordinating effect of air on rare earth metals is strongly dependent on the nature of the latter. Europium oxidizes almost as vigorously as sodium. Lanthanum and neodymium oxidize rather quickly (in dry air at room temperature at a rate of 1 to 100 mg / dm<sup>2</sup> per day). The oxidation rate increases strongly with moderate heating, and the presence of water vapor (75% relative humidity) increases the oxidation rate at any temperature by approximately one order of magnitude. Other rare earth metals are much more stable. The rate of their oxidation in dry air at room temperature is very low, but it increases significantly with heating (at temperatures above 200 °) or in humid conditions at temperatures around 1000. Samarium is highly stable in dry air, and with an increase in temperature from 200 to 6000 daily corrosion increases from 35 mg / dm<sup>2</sup>.

In the work of Lee Linda and Green [12], metals of high purity (99.9%) were used for the study. The oxidation rate of the samples was determined in dry and moisture-saturated air. The results obtained are in good agreement with the data of Love [11] (slightly lower corrosion rates in [12] are explained by the higher purity of the materials used in this work).

The mechanism of metal oxidation at high temperatures, according to Vorres and Iring [13], is determined by the diffusion of oxygen through the oxide layer. Such a mechanism seems to be quite probable, since in all cases the formed oxides had a fluorite structure, and the migration of anions in a lattice of the fluorite type, apparently, occurs so intensively that it almost suppresses the movement of cations.

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On the basis of the considered data on the rate of oxidation of metals, one can also come to the conclusion that the rate of corrosion depends to a large extent on the purity of the metals.

The influence of moisture, which greatly increases the rate of corrosion, according to Love [11], is reduced primarily to a change in the nature of the initially formed oxide film. However, both in Love's work and in other works [12, 13], data on the structure of the oxide film and the composition of the phases formed are not presented.

At certain pressures, the rate of oxygen delivery to the oxidized surface, due to diffusion in the gas phase, is greater than the rate of the oxidation reaction at the metal-oxygen phase boundary and the rate of oxygen

diffusion through the reaction product. This makes it possible to study the oxidation of metals at reduced pressure, which increases the accuracy by reducing convection flows in the system.

After the appearance in 1925-1928. of works by Goldschmidt and co-workers [2, 14, 15], the concept that rare earth sesquioxides crystallize in three polymorphic structural forms: cubic (C), monoclinic (B), and hexagonal (A), and crystallization in one or another structural form is entirely determined by the temperature and the size of the ionic radii of the rare earth elements.

According to Goldschmidt, the hexagonal form (A), which is stable at the highest temperatures, can be obtained for the oxides La, Ce, Pr, and Nd. The cubic form (C), stable at low temperatures, can be obtained for all oxides of rare-earth elements, except for the four mentioned, which have the largest ionic radii. Between the A and C forms, a less symmetrical B form may form. Thus, oxides of the elements Pr, Nd, Sm, Eu, Gd, and Dy were obtained by Goldschmidt in a pseudotrigonal structure (Bi-form). In addition, for the oxides Sm, Gd, and Nd, another crystalline form was also observed, designated by him as B2 and probably related to the trigonal type of structure.

It was found that the region of stability of individual structural types changes in the lanthanum-lutetium series, thus, the transformation temperature increases with an increase in the atomic number or, which is the

same, with a decrease in the ionic radius of elements. It was also assumed that the phase transformations are completely reversible with a change in temperature.

However, already in 1935, Loberg's work appeared, in which it was reported about the preparation of the C-form of  $\text{La}_2\text{O}_3$  and  $\text{Nd}_2\text{O}_3$  [3]. Soon, the C-form was obtained for praseodymium oxide [8], as well as data on the possibility of obtaining the C-form of  $\text{Ce}_2\text{O}_3$  in a highly reducing environment. Thus, the C-form was obtained for all oxides of rare earth elements. In later works, the B-form was not found in neodymium and praseodymium oxides, and the existence of two different low-symmetry crystal structures (B1 and B2) in samarium and gadolinium oxides was also questioned [3, 7, 8, 16, 17, 18, 19]. For example, Kuentert and Mozzi [17], in order to determine whether the B1 and B2 forms of  $\text{Gd}_2\text{O}_3$  exist, studied the transition of low-temperature cubic gadolinium oxide to the high-temperature B-form. It was shown that the C-form directly transforms into the monoclinic, which is isomorphic to the B-form of  $\text{Sm}_2\text{O}_3$ , the B2-form was not found.

Table 1 shows the temperatures of obtaining various modifications of sesqui rare-earth oxides, according to the data of Yandeli [8]. The firing time was 96-120 hours at 5000, 6-7 hours at 10,000 and 1-2 hours at a higher temperature.

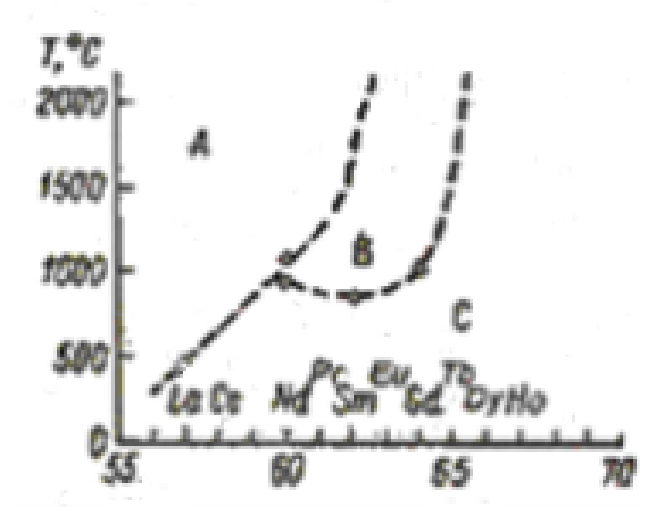
**Table 1. Obtaining modifications A, B and C sesquioxides [8]**

Oxide	Obtaining temperature, o, C
C- +A- La <sub>2</sub> O <sub>3</sub>	350, 450, 500
A - La <sub>2</sub> O <sub>3</sub>	600, 1000
C - Pr <sub>2</sub> O <sub>3</sub>	500, 600
A - Pr <sub>2</sub> O <sub>3</sub>	700, 850, 1000, 1100
C – Nd <sub>2</sub> O <sub>3</sub>	600, 700, 775
A - Nd <sub>2</sub> O <sub>3</sub>	850, 1000, 1200
C – Sm <sub>2</sub> O <sub>3</sub>	500, 1000, 1100
B - Sm <sub>2</sub> O <sub>3</sub>	1200, 1300, 1400
C – Eu <sub>2</sub> O <sub>3</sub>	500, 900, 1000, 1300
B - Eu <sub>2</sub> O <sub>3</sub>	1400
C – Gd <sub>2</sub> O <sub>3</sub>	500, 1000, 1300, 1500
C – Tb <sub>2</sub> O <sub>3</sub>	500, 1000, 1400
C – Dy <sub>2</sub> O <sub>3</sub>	500, 1000, 1400

In the works of various authors, Goldschmidt's position on the reversibility of phase transformations in rare-earth oxides with a change in temperature was verified. Yandeli [8], Wolf and Bernighausen [7] could not establish, despite numerous repetitions and long exposures, in no case of a reversible transition of modifications C and A.

Schaefer and Roy [6] tried to find out the stability of oxides and hydroxides of rare-earth elements by studying phase equilibria in

systems of rare-earth element oxide — water. Considering that at a low partial pressure of water vapor, the activation energy for the formation of a new structure from a structure obtained at high temperatures is very high, which can manifest itself in the formation of amorphous or metastable phases, as well as in obtaining incorrect values of the equilibrium temperatures of phase transformations, Schafer and Roy carried out their experiments at high pressure of water vapor. The scheme of polymorphic transformations, according to their data, is shown in Fig. 3.



However, it should be remembered that these data were obtained under equilibrium and close to equilibrium conditions and cannot be compared with the results obtained by other methods.

Roth and Schneider [4] collected extensive material on rare-earth oxides, revised Goldschmidt's assumptions about the mechanism of polymorphism, and questioned the conclusions of Loberg, Roy and Schafer about the existence of reversible polymorphic transformations in the oxides under consideration.

In their studies, Roth and Schneider used reagents containing 99.9% of the main compound, with the exception of samarium oxalate, which contained 1% Eu, and neodymium oxide, which contained about 2% of various impurities. Up to an experiment temperature of 1650 °C, the samples were placed in an oven in a platinum crucible (or hung on a platinum wire), at a temperature above 1650 °, in an iridium crucible. After firing, the samples were quenched and subjected to X-ray analysis at room temperature. Some experiments were carried out in a vacuum

(with cerium and praseodymium oxides) and under hydrothermal conditions (with neodymium oxide).

The use of rare earth metals in industry gives a great technical and economic effect with the right choice of the scope:

- 1) It becomes possible to create new materials with an increased complex of physicochemical properties. This primarily refers to the use of individual REM, their alloys and compounds;
- 2) The use of small additives of relatively cheap REM ligatures with other metals or oxides and other REM compounds causes a sharp increase in product quality, the percentage of product yield, a significant simplification and cost reduction of the technological process and an increase in productivity. This is especially important for metallurgy in the production of cast iron, steel, non-ferrous metal alloys, heat-resistant alloys, glass industry (production of quality glass), as well as in the chemical industry. The use of rare earth metals in metallurgy in the form of small additives is based on their high affinity for oxygen,



sulfur, hydrogen, phosphorus, and arsenic, the impurities of which impair the properties of steels and alloys. Interacting with these impurities, REM bind them into refractory compounds and dramatically improve the mechanical properties of cast iron, steel, etc. non-ferrous metal alloys. In addition, REM refines the grain size of metallic materials and thereby also increases the mechanical properties.

REM additives dramatically improve the mechanical properties, especially the ductility of most steel grades, and increase the yield of useful products. REM have the prospect of being used in cast carbon, low-alloy structural, stainless, heat-resistant, austenitic, silicon, automatic, tool steels and in alloys for heating elements. The most effective are the addition of rare earth metals to high-quality steel.

In non-ferrous metallurgy, alloying of magnesium alloys with rare-earth metals provided the production of new heat-resistant materials used up to temperatures of 250-300 °. In addition, rare-earth metals increase the casting characteristics of magnesium alloys (fluidity increases and porosity decreases). The alloying of REM alloys based on aluminum has not yet been sufficiently studied.

Rare earth metals are very effective in the form of small additions to almost all refractory metals used as the basis of heat-resistant alloys. Experimental data show that in almost all metals, which are the basis of industrial alloys, the solubility of rare earth metals in the solid state is tenths or hundredths of a percent. The only exceptions are magnesium, chromium, and titanium, which can dissolve some rare earth metals in the range of 1-3%. This nature of the interaction of rare-earth metals

with base metals shows that their small additives should be used in metallurgy. Practically, with the exception of magnesium and aluminum alloys, the addition of rare earth metals in metallurgy does not exceed 0.5–1.0%, and sometimes they are even less.

## CONCLUSION

REM affect the properties of other metals and alloys as follows:

- 1) Grinding of crystals of the base of the alloy - pure metal or a solid solution based on it;
- 2) Refining from metalloids impurities that cause brittleness of alloys, such as oxygen, nitrogen, hydrogen and carbon.
- 3) The formation of refractory compounds with harmful impurities and the elimination of low-melting eutectic inclusions that cause red brittleness (sulfur, phosphorus, arsenic in steel; lead and bismuth in copper alloys), i.e. the property of the alloy to give cracks during hot working with pressure (forging, stamping, rolling) in the temperature range of red or yellow heat;
- 4) Improvement of the structure of the surface oxide film, causing a sharp increase in the heat resistance of alloys;
- 5) Changing the mechanism of plastic deformation of the alloy base;
- 6) An increase in the temperature of recrystallization of the alloy;
- 7) Hardening of the alloy by alloying the solid solution or the formation of new compounds, as well as their redistribution during heat treatment;
- 8) Imparting special physical properties to alloys, for example, a sharp increase in the neutron capture cross section due to the introduction of gadolinium additives, etc.

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