

## SYSTEMS OF RARE EARTH ELEMENTS

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### I. INTRODUCTION

Modification of systems by introducing of rare earth elements (REE) allows you to purposefully change the properties of materials.

The most important application areas of REE are petrochemicals, electronics, glass and ceramic industries. For example, polycrystalline ceramics  $Y_3Al_5O_{12}$  (YAG) is used for the production of YAG-SiC nanocomposites with finely dispersed microstructures. The combustion synthesis after calcination at 1000 °C is presented in [1].

Wide-band gap aluminate phosphors  $MeAl_2O_4:Eu_2+Re$ , where Me is an alkaline earth metal, Re is an element from the REE group, have high light accumulation properties, high brightness of residual afterglow sufficient for daily observation of glow in the dark. Their operational life is not physically limited [2]. The innovative technology of continuous synthesis proposed by the authors for the synthesis of strontium aluminates will allow obtaining ultra- and nanoscale phosphor powders directly within the synthesis process; reducing the temperature and duration of the synthesis due to the thermal shock and the use of special glass additives; optimizing the granulometric composition of synthesized powders.

In work [3], an effective, technological method for improving the properties of foundry heat-resistant alloys by microalloying REE (cerium, yttrium, lanthanum, scandium) is presented.

The successful creation of new functional materials based on REE and development of production technology requires the creation of technologies for obtaining lanthanides in pure form. To solve these problems, REE systems are being investigated [4-8].

The purpose of the work is to study trichloroacetates of water-salt REE systems, to establish the regularities in the behavior of solubility branches and in the nature of component interaction and to calculate the thermodynamic characteristics of solid solutions.

### II. MATERIALS AND METHODS

The literature data on the study of the systems of chlorides, nitrates, iodides, sulfates, selenates, bromates, ethyl sulfates of REE allow us to compare not only the behavior of the salts of the same anion in the REE series, but also to consider the effect of the anion on the behavior of salts with the same cations.

The most frequent are continuous series of solid solutions. Of the nine systems of REE ethyl sulfates studied in six, solid solutions are formed [9]. In systems of REE bromates, solid solutions are also predominantly formed [10].

To determine the regularities in the distribution of components between phases, the systems  $Ln_1(CCl_3COO)_3 - Ln_2(CCl_3COO)_3 - H_2O$  at 298 K, where Ln is the cation of the rare-earth element, are studied. Trichloroacetates REE are crystalline hydrates with a variable content of crystallization water. Trichloroacetates of lanthanum, neodymium, and samarium crystallize with six and three water molecules. Trichloroacetate praseodymium, yttrium, holmium, erbium, dysprosium crystallize with three water molecules.

The composition of salts is determined by chemical analysis. A rare-earth element was determined by complexometric titration with Xylenol Orange [11], and the chlorine content was estimated by organoelement analysis via the combustion of a sample in a microbomb with metallic sodium and subsequent titration of chloride ion [12]. The number of water molecules was found by difference and by differential thermal analysis.

The mutual solubility of salts of rare-earth elements in systems has been studied by isothermal solubility. The equilibrium between the liquid and solid phases was achieved as a result of recrystallization. The time to reach equilibrium was 7 days. The equilibrium liquid phase is separated from the solid phase by means of filter No. 3. The resulting liquid phase and solid residues were analyzed. The equilibrium moment is determined by the constancy of the composition of the liquid and solid phases in time and the constancy of the refractive index, measured on a Refractometer RL-1. All investigations and measurements were carried out at a temperature of 298 K.

Analysis of the distribution diagrams (Figure1) shows that in the  $Nd(CCl_3COO)_3 - Ln(CCl_3COO)_3 - H_2O$  systems, where Ln is Pr, Y;  $Sm(CCl_3COO)_3 - Y(CCl_3COO)_3 - H_2O$ ,  $Gd(CCl_3COO)_3 - Er(CCl_3COO)_3 - H_2O$  the solid phase is enriched with a less soluble component in the entire concentration range. In the Ho-Er

system, enrichment of the less soluble  $\text{Ho}(\text{CCl}_3\text{COO})_3$  component leads to 65 mol% of the erbium trichloroacetate content in the liquid phase, with an increase in its content in the liquid phase, the solid phase is enriched in  $\text{Er}(\text{CCl}_3\text{COO})_3$ . The solubilities of  $\text{Nd}(\text{CCl}_3\text{COO})_3$  and  $\text{Sm}(\text{CCl}_3\text{COO})_3$  are similar and comprise, 60.80 and 60.40 wt.%. When the content of  $\text{Nd}(\text{CCl}_3\text{COO})_3$  in the liquid phase is up to 51 mol%, the solid phase is enriched in  $\text{Sm}(\text{CCl}_3\text{COO})_3$ , with a larger content of  $\text{Nd}(\text{CCl}_3\text{COO})_3$ .

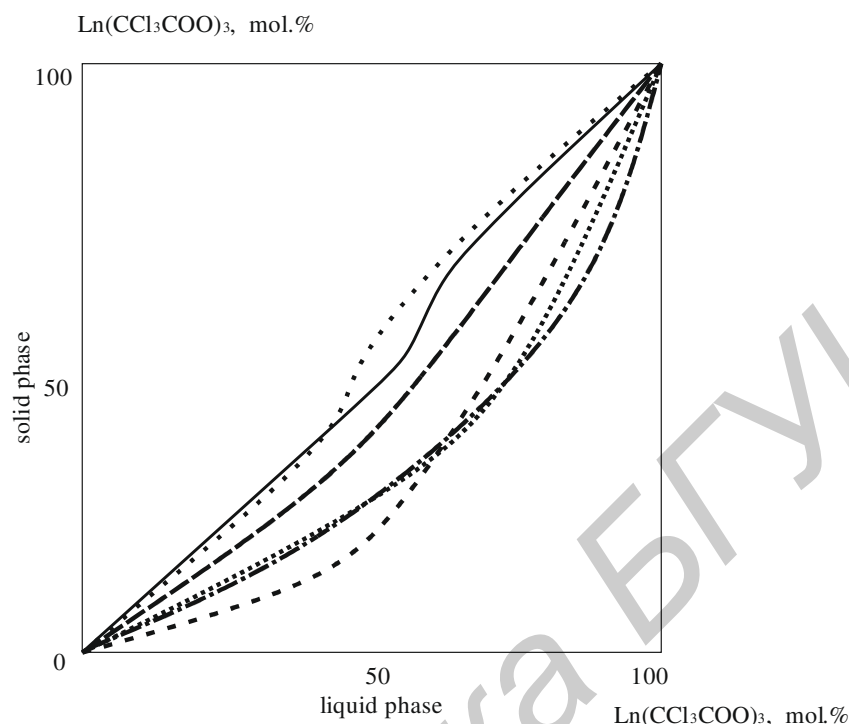


Figure 1 – The distribution diagrams of the systems

.....  $\text{Pr}(\text{CCl}_3\text{COO})_3\text{-Nd}(\text{CCl}_3\text{COO})_3\text{-H}_2\text{O}$ ;    · · · ·  $\text{Nd}(\text{CCl}_3\text{COO})_3\text{-Sm}(\text{CCl}_3\text{COO})_3\text{-H}_2\text{O}$   
 - - -  $\text{Gd}(\text{CCl}_3\text{COO})_3\text{-Er}(\text{CCl}_3\text{COO})_3\text{-H}_2\text{O}$ ;    —  $\text{Ho}(\text{CCl}_3\text{COO})_3\text{-Er}(\text{CCl}_3\text{COO})_3\text{-H}_2\text{O}$   
 - - -  $\text{Nd}(\text{CCl}_3\text{COO})_3\text{-Y}(\text{CCl}_3\text{COO})_3\text{-H}_2\text{O}$ ;    - - -  $\text{Sm}(\text{CCl}_3\text{COO})_3\text{-Y}(\text{CCl}_3\text{COO})_3\text{-H}_2\text{O}$

The coefficients of activity were calculated for the components of solid solutions.

An analysis of the change in the activity coefficients of the components shows that there is a region of pseudo-ideal solutions in the system. The coefficients of the main component are equal to unity, the activity coefficients of the second component are greater than one.

Solid solutions of trichloroacetate praseodymium-neodymium, neodymium-yttrium are close to ideal. Solid solutions of trichloroacetate neodymium-samarium, holmium-erbium, samarium-yttrium, neodymium-yttrium have a negative deviation of excess free energy from ideality. Solid solutions of gadolinium -erbium trichloroacetates deviate in a positive direction from ideality.

### III. RESULTS AND DISCUSSION

The complication of the composition, the increase in the mass and size of the anion results in a smoothing of the relative differences in the lattice of the components, a reduction in the energy expenditure on the deformation of the crystal lattice, so that the limits of isomorphous substitution can be extended. This is consistent with the provisions of the energy theory of isomorphism proposed by Urusov [13]: the enthalpy of mixing of the solid solution is proportional to the square of the relative difference of the interatomic distances ( $\Delta r$ ), which decreases with increasing anion with a fixed value of  $\Delta r$ .

The asymmetric dependence of the energy of formation of solid solutions on composition is related to the difference in the dimensions of the co-crystallizing components.

With a negative deviation from ideality, solid solutions are formed on the basis of a less soluble component, which possesses large parameters of the crystal lattice. The entry into the crystal lattice of a smaller ion leads to a decrease in the coefficients of the activity of the components and to a negative deviation from ideality.

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## APPROACHES FOR SUBSTRATE SURFACE FUNCTIONALIZATION WITH AgNPs

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### I. INTRODUCTION

Metals have a long history in the treatments of dentistry and orthopedics. Pure titanium is commonly used as artificial joints and implants in both dental and orthopedic clinics because of its biocompatibility and mechanical properties. A major factor that determines the success of dental implantation is osseointegration, which is the stable anchorage of an implant in living bone achieved by direct bone-to-implant contacts [1, 2]. It is commonly known that the implantation of a foreign object into the human body may be rejected. Moreover, a wide range of local tissue reactions, in particular inflammation, giant cell formation and fibrosis can be induced [3]. Consequently, the task of biomedical materials science is the formation of biocompatible and antibacterial implant surfaces for medical use. Besides necessary to formation the structural and functional connection between organised vital bone and the surface of a titanium implant, capable of bearing the functional load [4]. Furthermore, biomaterials should support cell attachment, migration, proliferation, interact actively with cells and tissues and stimulate regeneration [5], which allows to avoid rejection and speed up the treatment and recovery process [6, 7]. Films composed of noble metal nanoparticles (typically, Au or Ag) currently have attained wide popularity and aroused intense research interest in nanotechnology. The most recently available methods for the fabrication of antibacterial films include electron beam lithography and nanoimprint lithography, both can completely control the micromorphology of the nanostructures for the design with unique localized surface plasmon resonance spectrum [8, 9]. However, these methods require sophisticated fabrication equipment and are limited by either expensive cost or small sample size in practical applications. Instead, some simpler bottom-up approaches based on self-assembly, e.g., Langmuir-Blodgett, dip coating, and electrochemical deposition, have shown great conveniency in large-scale fabrication and much less defectivity [10, 11]. Such techniques can surely produce noble metal nanoparticle thin films with large areas.

The paper considered a series of rapid and simple methods of silver coatings fabrication such as dip coating, sessile drop and room temperature electrophoretic deposition (EPD).

### II. EXPERIMENT DESCRIPTION

According the results of [12-14] the negatively charged AgNPs were synthesized by wet chemical reduction method of silver nitrate (Fluker, p.a.) using glucose (D-(+)-glucose, Baker) as a reductant and polyvinylpyrrolidone (PVP K30 Povidon 30; Fluka, molecular weight 40000 g mol<sup>-1</sup>) as a stabilizer. Initially 2 g glucose and 1 g PVP were dissolved in 40 g water and heated to 90 °C. Then 0.5 g AgNO<sub>3</sub> dissolved in 1 mL water was quickly added. The dispersion was kept at 90 °C for 1 h, PVP-stabilized AgNPs and then