High entropy oxide systems based on rare earth elements

V I Sachkov¹, R A Nefedov¹ and I V Amelichkin¹
¹Innovation and Technology Center, National Research Tomsk State University, 36 Lenin Street, Tomsk 634050, Russian Federation

E-mail: amelichkinivan@gmail.com

Abstract. In this paper we synthesized high entropy oxide system (Sc₀.2Ce₀.2Pr₀.2Gd₀.2Ho₀.2)₂O₃±δ by precipitation of hydroxides from REE nitrates aqueous solutions and annealing the mixture at 800 °C. It is possible to obtain the various forms of simple and complex composition based on the rare earth oxides, including oxides in the form of nanosized powders. The main idea of obtaining HEOS comes from the field of high-entropy alloys. The interconnection between configurational entropy and mixing enthalpy is a key factor for determining phase transformations. The phase composition, structure, and surface morphology of the obtained powders were investigated by scanning electron microscopy and X-ray phase analysis methods.

1. Introduction

High entropy oxide systems (HEOS) are systems that contain more than three components with a uniform distribution of ions in crystal lattice. Such systems are characterized by increased entropy of mixing [1,2].

The main idea of obtaining HEOS comes from the field of high-entropy alloys (HEA). HEAs have a number of important mechanical (strength, hardness, plasticity, wear resistance), physical (magnetic, conductivity) and chemical (corrosion resistance) properties compared to conventional alloys with one or two basic elements. In such metal systems, high mixing entropy thermodynamically stabilizes a single-phase solid solution by reducing the Gibbs free energy. By analogy with HEAs, it can be expected a similar entropy mixing effect in oxide systems. HEOS can be used as adhesive protective coatings, optical processors, waveguides, radiopaque substances, catalysts, luminescent compounds, multiferroics, acousto-optic, data storage and reading devices [3,4].

One of the important areas of modern research in the field of HEOS synthesis and materials based on them is the development and improvement of specific methods for their preparation. The choice of methods for the synthesis of such materials influences on the composition, structure, particle size and determines the technological effectiveness of the process for their preparation. Prospective compared with high-temperature methods of solid-phase synthesis are the methods of ‘soft chemistry’ or solution methods, for example, the sol-gel method [5]. In the latter case it is possible to obtain the various forms of simple and complex composition based on rare earth oxides, including oxides in the form of nanosized powders.

This work is focused to explore the possibility of obtaining of high entropy oxide powders based on rare earth elements (REE) by hydroxides precipitation from nitrates solution.

2. Experimental part
Synthesis of HEOS based on REE can be divided into five stages (figure 1). As starting materials were used: Sc(NO$_3$)$_3$·4H$_2$O, Ce(NO$_3$)$_3$·6H$_2$O, Pr(NO$_3$)$_3$·6H$_2$O, Gd(NO$_3$)$_3$·5H$_2$O, Ho(NO$_3$)$_3$·5H$_2$O, NaOH.

**Figure 1.** General flowchart of synthesis steps.

Consider the following example of synthesis HEOS ($\text{Sc}_{0.2}\text{Ce}_{0.2}\text{Pr}_{0.2}\text{Gd}_{0.2}\text{Ho}_{0.2}$)$_2$O$_{3±δ}$ with a theoretical yield of the product in an amount of 1.2 g.

The first stage is the mixing of aqueous solutions of REE nitrates. One of the conditions for obtaining HEOS is equal mole ratio of each component in the system. The aliquot volume ($V_a$) was calculated based on the concentrations of REE nitrates and the number of moles (0.002). The concentrations of initial solutions and the volumes of aliquot ($V_a$) are listed in table 1.

| REE nitrates        | Concentration (mmol/ml) | $V_a$ (ml) |
|----------------------|-------------------------|------------|
| Sc(NO$_3$)$_3$·4H$_2$O| 0.330                   | 6.060      |
| Ce(NO$_3$)$_3$·6H$_2$O| 0.229                   | 8.700      |
| Pr(NO$_3$)$_3$·6H$_2$O| 0.230                   | 8.680      |
| Gd(NO$_3$)$_3$·5H$_2$O| 0.230                   | 8.660      |
| Ho(NO$_3$)$_3$·5H$_2$O| 0.226                   | 8.820      |

The solutions were mixed in a 250 ml beaker on a magnetic stirrer for one hour at the room temperature.

The second stage is the precipitation of hydroxides from a mixture of nitric acid solutions of REE. Precipitation process may be described by the chemical reaction:

$$\text{Me(NO$_3$)$_3$} + 3\text{NaOH} \rightarrow \text{Me(OH)$_3$}↓ + 3\text{NaNO$_3$},$$

where Me = Sc, Ce, Pr, Gd, Ho.

The precipitation was carried out with a solution of NaOH, which was intensively mixed on a magnetic stirrer. The volume of NaOH solution taken with a 10% excess for the complete precipitation of REE hydroxides mixture of this system was calculated based on maximum pH of precipitation of the mixture.
hydroxides from the REE nitrates solution in the system. The excess solution of NaOH was calculated by multiplying the stoichiometric weight amount by the accepted amount of its excess. To reduce the reaction time, it is necessary to pour a mixture of nitric acid solutions of REE into the NaOH solution with vigorous stirring. This method is conventionally called the "reverse" method of synthesis. The solution resulting from mixing with the precipitate of REE hydroxides was incubate for two hours at room temperature.

The third stage is rinsing the solution with distilled water to pH = 8. The pH measurement was performed by a potentiometric method on a pH-150MI device. The solution became turbid with stirring. The resulting suspension was left to settle for precipitation to the bottom. After settling, the upper transparent layer was decanted, distilled water was added and stirred. After precipitation, the upper layer was decanted again and rinsed. The necessity of such rinses is due to the presence of nitrate ions in the precipitate. The volume of distilled rinsing water was more than 500 ml. The presence of nitrate ions was determined by qualitative reaction with diphenylamine. In this case, initially, colorless diphenylbenzidine is formed, which upon further oxidation turns into a quinoid derivative of diphenylbenzidine having a blue color.

The fourth stage - filtering solution. The filtration process was performed using a Buchner funnel and a Bunsen flask on a blue-ribbon filter. The total rinsing and filtration time were 8 hours.

The fifth stage is drying and annealing a gel-like mixture of REE oxides. Drying was carried out in cupboards at a temperature of 70 °C for 12 hours. Annealing was carried out in muffle furnaces at a temperature of 800 °C for one hour. The practical yield of oxides was 97–99% of the theoretical. The method of "direct" synthesis included similar stages as the method of "reverse" synthesis, but in the second stage, on the contrary, the NaOH solution was poured into a mixture of nitric acid REE solution.

To study phase composition X-ray diffraction analysis (XRD) ‘DRON-3M diffractometer’ and scanning electron microscopy (SEM) ‘QUANTA 200 3D FEI’ with X-ray energy dispersive microanalysis system were used.

3. Results
The structural properties of \((\text{Sc}_{0.2}\text{Ce}_{0.2}\text{Pr}_{0.2}\text{Gd}_{0.2}\text{Ho}_{0.2})_2\text{O}_{3±δ}\) were investigated by XRD over 2θ range from 15° to 95° using a small step size (0.2°) and Cu-Kα radiation with a wavelength of 0.154 nm (figure 2).

![Figure 2. XRD pattern of HEOS (Sc0.2Ce0.2Pr0.2Gd0.2Ho0.2)2O3±δ.](image-url)
The XRD graph showed strong peaks at 28.5, 33.0, 47.4, 56.2, 59.0, 69.3, 76.5, 78.9, 88.3 degrees of 2θ. All the synthesized oxide nanoparticles diffraction peaks corresponded to (111), (200), (220), (222), (400), (311), (400) and (422) crystal planes. The average crystallite sizes of (Sc0.2Ce0.2Pr0.2Gd0.2Ho0.2)2O3±δ were determined based on the width of dominant peaks using the Scherrer equation, and they were in the range of 13.4 – 15.7 nm. The obtained XRD patterns obtained of the (Sc0.2Ce0.2Pr0.2Gd0.2Ho0.2)2O3±δ were compared with the standard data for CeO2 (JCPDS file No. 34-0394). The characteristic peaks are very close to the face centric cubic CeO2 indicating that all samples can be identified to ceria with the cubic fluorite structure. The lattice parameters of the prepared (Sc0.2Ce0.2Pr0.2Gd0.2Ho0.2)2O3±δ sample were determined to be 0.54181 nm. This lattice parameters are almost the same with the standard of CeO2 (0.54111 nm) [6].

The chemical composition of the prepared (Sc0.2Ce0.2Pr0.2Gd0.2Ho0.2)2O3±δ oxide powders was determined using energy-dispersive X-ray spectroscopy (EDS); the results are shown in figure 3. The EDS spectra clearly indicated that all of REE ions were present in sample.

**Figure 3.** EDS spectra of HEOS (Sc0.2Ce0.2Pr0.2Gd0.2Ho0.2)2O3±δ.

**Figure 4.** SEM image of morphology (a) and the distribution of elements on the sample surface.
According to the data of SEM, the sample under study is a loose powder with a developed surface morphology, which is represented by structural units in the form of spherical and oval particles, irregular polyhedrons and scales. All REE elements in the system are equally distributed over the sample surface (figure 4).

4. Conclusion
High entropy oxide system based on rare earth elements was successfully synthesized. The phase composition, structure, and surface morphology of the obtained powders were investigated by XRD, EDS and SEM methods. The lattice parameters of the prepared \((\text{Sc}_{0.2}\text{Ce}_{0.2}\text{Pr}_{0.2}\text{Gd}_{0.2}\text{Ho}_{0.2})_2\text{O}_{3+\delta}\) sample were determined to be 0.54181 nm. This lattice parameters are almost the same with the standard of \(\text{CeO}_2\) (0.54111 nm).

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