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Abstract

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INTERACTION OF Nd_2O_3 WITH WATER

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The rate of moisture absorption by the oxides of rare-earth elements at different relative humidities of the air was determined by Lave ([1]). However, Lave' s work did not investigate the composition and structure of the products obtained. Indications of the formation of amorphous hydroxyoxides of various compositions are given in ([2,3]). It is known that neodymium hydroxide crystallizes in a hexagonal structure ([4]). The data on the stability range of $Nd(OH)_3$ and its decomposition to the oxide, however, are contradictory ([3,5]). Shafer and Roy, studying the polymorphism of rare-earth oxides, were the first to become interested in the stability of hydroxides and oxyhydroxides at different water-vapor pressures. On the basis of the data obtained ([6]), they concluded that neodymium oxide can be obtained in three polymorphic modifications (A, B, C) and that transitions from one crystalline form to another are reversible. Somewhat later, Uorrou and Roy ([7]) confirmed the reversibility of the A—C transition of neodymium oxide under hydrothermal synthesis conditions, but they were unable under these conditions to obtain the intermediate B-form of Nd_2O_3.

Our work on the study of the neodymium oxide—water system included: 1) preparation of neodymium oxide hydrates by hydrothermal synthesis, 2) interaction of neodymium oxides with water at different temperatures and different relative humidities; 3) determination of the stability ranges and structure of hydrated neodymium oxides.

The behavior of neodymium oxides (A- and C-forms) with respect to water vapor was studied with the relative humidity varied from 25 to 95%. It was found that at 35° the A-form of Nd_2O_3 remains stable with respect to water vapor, whereas the C-form actively absorbs it, transforming into the hydrate $3Nd_2O_3 \cdot 2H_2O$. At temperatures of 90—100° a change is observed in the activity of the interaction of neodymium oxide with water: regardless of the relative humidity, equilibrium is already reached in 5 hours, with C-Nd_2O_3 converting into $3Nd_2O_3 \cdot 2H_2O$, while A-Nd_2O_3 forms $Nd_2O_3 \cdot 3H_2O$. It may be assumed that the activation energy of the hydration process of the C-form is very small, so that the reaction C-$Nd_2O_3 + (H_2O)_{gas} \rightarrow 3Nd_2O_3 \cdot 2H_2O$ can already proceed at room temperature. In view of the fact that the transition from the A-form into the hydrate requires a more profound change in structure, the activation energy

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of the reaction $A\text{-}Nd_2O_3 + (H_2O)_{gas} \rightarrow Nd(OH)_3$ is greater and, consequently, the hydration process begins at a higher temperature.

When the C-form of neodymium oxide is heated in moist oxygen in the temperature interval 100—400°, an increase in the weight of the specimens and a distortion (expansion) of the crystal lattice are observed. It might be supposed that under these conditions a neodymium oxide richer in oxygen than the sesquioxide is formed. It was precisely this reason that was invoked ([8]) to explain the increase in the lattice parameter of cubic Nd_2O_3 during storage in air. In order to check this phenomenon, thermogravimetric measurements were carried out in a stream of carefully dried oxygen and argon, and of moist oxygen and argon. In the preparations obtained, the content of active oxygen was determined, the magnetic properties were measured, and high-temperature X-ray analysis was performed. As a result of these investigations it was shown that the increase in the lattice parameters, occurring both in an atmosphere of moist oxygen and in moist argon, is not associated with the formation of higher neodymium oxides.

As can be seen from Figs. 1 and 2, when the C-form of neodymium oxide is heated in a stream of moist argon, an increase in the weight of the specimens begins already at 50—60°, associ-

ous, with formation of a hydrate of composition $3Nd_2O_3 \cdot 2H_2O$; above 300° it decomposes, releasing water and converting into the C form. An endothermic effect is observed on the thermograms in this process. When heated at a rate of 100° per hour, decomposition is complete by 400°. On cooling in a stream of moist gases, formation of $3Nd_2O_3 \cdot 2H_2O$ is again observed. The processes of formation and decomposition are completely reversible, and on heating at the indicated rate the hysteresis does not exceed 100°.

Fig. 1. Change in weight of samples of neodymium oxide when heated to 1300° in a stream of moist argon (in wt.%): 1—A form, 2—C form, compound $3Nd_2O_3 \cdot 2H_2O$.

When the C form of neodymium oxide was heated in the region of the phase transition, a further change in the weight of the samples was found. The cause of this, as was established, was the evolution of water. Thus, the conversion of the C form of the oxide into the A form is in reality the decomposition of a compound containing water. It is precisely the fact that this water enters the crystal lattice that allows it to remain in the structure up to such high temperatures as 800—1000°. The established nature of the C→A transition makes it possible to explain the fact that arbitrarily long holding at different temperatures in dry air or oxygen cannot convert the A form of neodymium oxide into the C form. Only under hydrothermal-synthesis conditions, when the pressure of water vapor is sharply increased, is conversion of the A form into the C form possible.

To clarify the stability region of $Nd_2O_3 \cdot 3H_2O$, thermogravimetric, thermoanalytical, and X-ray studies were carried out. Decomposition of the oxide hydrate in air begins at a temperature of $\sim 250°$ and proceeds in two stages. The first endothermic effect, with a maximum at 350—400°, corresponds to the formation of the basic hydrate $Nd_2O_3 \cdot H_2O$, crystallizing in low symmetry. It is stable up to 450°; above this temperature it decomposes, forming the C form of neodymium oxide, i.e., a hydrate of composition $3Nd_2O_3 \cdot H_2O$. The latter at higher temperatures (800—1000°) is converted, with release of water, into hexagonal neodymium oxide (A form).

To determine the structure of the compounds, as well as the nature of the water bound with the oxides, IR absorption spectra in the range 400—4000 cm^{-1} were studied for both hydrated and deuterated preparations, and X-ray analysis was performed. The IR spectra were measured on IKS-12 and IKS-14 spectrometers. X-ray patterns were recorded by the powder method in VRS-3 cameras with a cassette diameter of 143.25 mm, using $Cu_{K\alpha}$ radiation.

In the Nd_2O_3—H_2O system we found the following chemical compounds: the trihydrate $Nd_2O_3 \cdot 3H_2O$, the monohydrate $Nd_2O_3 \cdot H_2O$, the compound $3Nd_2O_3 \cdot 2H_2O$, the C form of composition $3Nd_2O_3 \cdot H_2O$, and the A form Nd_2O_3.

The trihydrate is the hydroxide $Nd(OH)_3$ with an absorption band at 3604 cm^{-1}, corresponding to the stretching (ν_{OH}) vibration, and a band at 676 cm^{-1}, corresponding to the librational vibration of hydroxyl (δ_{OH}). In the lattice of neodymium hydroxide, as in lanthanum hydroxide, hydrogen bonding is absent or extremely weak. $Nd(OH)_3$ crystallizes in a hexagonal structure of the UCl_3 type, space group $C6_{3/m}$, with lattice constants: $a_0 = 6.42$ Å, $c_0 = 3.74$ Å.

In the compound $3Nd_2O_3 \cdot 2H_2O$, the water is also present in the form of hydroxyl groups, between which weak hydrogen bonding occurs. In the spectrum of the C form ($3Nd_2O_3 \cdot H_2O$), an absorption band of the stretching vibrations of hydroxyl groups is found with a maximum at 3416 cm^{-1}, as in the spectrum of $3Nd_2O_3 \cdot 2H_2O$. However, it is broader and has a complex contour. It may be assumed that at least some of the inclusions in the lattice of the C form

consists of structurally bound hydroxyl groups. The splitting of the frequency of the pendulum vibration δ_{OH} in the spectrum of $3Nd_2O_3 \cdot 2H_2O$, as well as the complex configuration of the bands in the region 540–420 cm^{-1} in the spectrum of $3Nd_2O_3 \cdot 2H_2O$ and the C-form, are possibly due to the lowered symmetry of the coordination sphere of the cation in the lattice and to the presence of both stronger and weaker Nd–O bonds.

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X-ray diffraction studies showed that both the C-form and $3Nd_2O_3 \cdot 2H_2O$ crystallize in cubic symmetry, with a lattice of the Mn_2O_3 type. Coordination numbers: $M_1 = 6$O (C-–), $M_2 = 6$O (C=), O $= 4M(T)$. Unit-cell parameters: for $3Nd_2O_3 \cdot 2H_2O$, $a_0 = (11.518 \pm 0.006)$ Å, and for the C-form, $a_0 = (11.080 \pm 0.008)$ Å.

It is known (^{9}) that the C-type structure of trivalent rare-earth oxides is very close to the structure of PrO_2 (CaF_2 type). The unit cell of C–Ln_2O_3 consists of 8 unit cells analogous to those of PrO_2, but in which 16 oxygen atoms have been regularly removed. Because of these vacancies, the metal atoms in the cell are slightly displaced from the positions they occupy in the PrO_2 structure. The positions of the remaining 48 oxygen atoms in the cell are also somewhat distorted. Thus, in the structures of PrO_2, C-type rare-earth oxides-

ions; in particular, in the C-form of neodymium oxide ($3Nd_2O_3 \cdot H_2O$) and in the compound $3Nd_2O_3 \cdot 2H_2O$, the cations occupy sites of the densest spherical packing, while the anions are located in tetrahedral voids. In oxides of the C type, owing to a deficiency of oxygen ions, as compared with PrO_2, some of the tetrahedral interstices remain unoccupied.

Precision determination of the unit-cell parameters of the C-form of neodymium oxide and of $3Nd_2O_3 \cdot 2H_2O$ made it possible to calculate the X-ray density of the substances; comparison of this with the pycnometric density makes it possible to judge the number of defects in the crystal lattice. Such a calculation, as well as data from molecular spectra, show that in the lattice of the C-form of neodymium oxide some of the vacancies of oxygen atoms are occupied by OH groups. These groups are arranged regularly, and each unit cell contains 8–10 OH groups, half of which occupy the sites of oxygen atoms, and the remainder the vacant tetrahedral voids. In the structure of the compound $3Nd_2O_3 \cdot 2H_2O$ (perhaps, more exactly, $4Nd_2O_3 \cdot 2H_2O$), the OH groups occupy half of the vacant tetrahedral voids (in all, the unit cell contains 16–18 OH groups).

The structure of the A-form of neodymium oxide has been examined in detail by Douglas (^{11}). The lattice is hexagonal, of the La_2O_3 type. Unit-cell parameters: $a_0 = 3.841$ Å, $c_0 = 6.002$ Å, $c/a = 1.564$. The neodymium atom is surrounded by seven oxygen atoms, four Nd–O distances of ~ 2.37 Å and three distances of 2.63 Å. The spectrum of A–Nd_2O_3 consists of an intense band at 510 cm^{-1} and a weaker band with a maximum at 420 cm^{-1}.

In considering the system involving neodymium oxide, one cannot fail to mention the proposition advanced by Roth and Schneider (^{10}) that the A type of rare-earth oxides is stable for large ions and the C type for small ions. Crystal-chemical and energetic considerations permit one to assert the thermodynamic instability of neodymium sesquioxide crystallized in the structure of the cubic C type.

By various methods of chemical analysis we have shown that the phase usually taken to be the C-form of neodymium oxide is in fact a hydrate of composition $3Nd_2O_3 \cdot H_2O$. This, however, does not exclude the possibility of obtaining the C-form of "pure" neodymium oxide under specially created conditions (for example, heating in a high vacuum), but in any case this form will be metastable, and the transition C → A will be monotropic.

The C-form of neodymium oxide can be stabilized by introducing impurities, for example, ZrO_2, CeO_2, H_2O. In the latter case, as we have shown, the compound $3Nd_2O_3 \cdot H_2O$ is formed, while in the case of additions of ZrO_2 and CeO_2, cubic solid solutions are formed. Both $3Nd_2O_3 \cdot H_2O$ and the solid solutions crystallize in the C-form of neodymium oxide and are stable up to a temperature of 800–1000°. When the temperature is raised above 1000°, the cubic solid solutions decompose. Cerium dioxide is reduced to Ce_2O_3 and forms a hexagonal solid solution with the A-form of Nd_2O_3; in the second case, part of the neodymium oxide combines with ZrO_2 in $Nd_2Zr_2O_7$, while the remainder transforms into the A-form of Nd_2O_3.

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Note: Figure translations are in progress. See original paper for figures.