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Electron-Diffraction Study of Neodymium Oxides

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The literature contains no data that describe sufficiently completely the process of oxidation of neodymium. As a first approximation, one might have assumed that neodymium and oxygen form compounds which, in composition and structure, are analogous to the oxides of cerium, praseodymium, and other rare-earth metals. On closer examination, however, this proved to be far from the case. It is known that all rare-earth elements form sesquioxides—Me_2O_3. As Jost et al. indicate ([1]), oxides of this composition are stable in air at room temperature. On red heat, however, of all the rare-earth elements only cerium, praseodymium, and terbium form compounds with a larger amount of oxygen.

There are, however, data ([2]) according to which, at room temperature, Ce_2O_3 is slowly oxidized to CeO_2, Tb_2O_3 to Tb_4O_7, Pr_2O_3 to Pr_6O_{11}, and only on fusion with sodium perchlorate—to PrO_2.

As regards the structural characteristics of the oxides of the rare-earth elements and their changes on heating in air, it is known that the sesquioxides of cerium, lanthanum, and praseodymium have hexagonal crystal lattices, while cerium dioxide (CeO_2) and praseodymium dioxide (PrO_2) are cubic. As Vickery established ([3]), the hexagonal modification of Pr_2O_3 changes into the cubic one, and only the latter, being oxidized in air at high temperatures, passes into praseodymium dioxide.

In contrast to the elements mentioned, terbium and oxygen form the cubic sesquioxide (Tb_2O_3), which on further oxidation passes into TbO_2. At present it is known ([4,5]) that neodymium sesquioxide can exist in the form of hexagonal and cubic modifications.

A higher degree of oxidation of neodymium to NbO_2 is not yet known. The literature likewise gives no temperature conditions for the oxidation of neodymium and does not describe the intermediate oxides formed. In order to study the processes of oxidation of neodymium, the present work used the method of fast-electron diffraction on thin oxidized neodymium films.

Evaporation of neodymium and condensation of its vapors in the form of a thin film suitable for electron-diffraction studies were carried out in a special apparatus in which a vacuum of 6—7 $\cdot 10^{-6}$ mm Hg was maintained. Since the rapidly flying neodymium atoms "burned through" the collodion film (substrate), a copper mesh (60–130 mesh), obtained electrolytically, was used to protect it.

The very thin film prepared from neodymium was placed in an electron-diffraction camera made ready for operation, where electron-diffraction patterns of neodymium not yet oxidized were immediately obtained. Then a thermocouple junction was attached to the copper mesh on which the neodymium film under investigation was located, after which they were heated in a furnace. The error in measuring the temperature of the mesh did not exceed 10–15°. Simultaneously, separate pieces of the neodymium film, for studying its oxidation in air, were kept at room temperature.

The electron diffraction pattern obtained from the initial neodymium film is shown in Fig. 1a. The data from its calculation at $2L\lambda = 42.0$ are given in the first three columns of Table 1. To identify the phase composition of the specimen, the subsequent columns contain the values of the interplanar spacings and intensities of the interference maxima, calculated by us from structural data (^{4,5}) for neodymium and its sesquioxide of the cubic modification.

Table 1

$2r$	I	d, Å	Neodymium I	Neodymium d, Å	Nd_2O_3 cub. I	Nd_2O_3 cub. d, Å
13.3	1.00	3.16	0.25	3.15	1.00	3.199
15.2	0.30	2.76	1.00	2.79	0.30	2.76
17.2	0.05	2.45	0.20	2.46	0.05	2.47
21.8	0.60	1.92	–	–	0.60	1.95
25.5	0.30	1.64	0.20	1.67	0.30	1.67
33.9	0.10	1.23	0.10	1.15	–	–
38.0	0.10	1.10	0.10	1.15	–	–
40.0	0.05	1.05	0.10	1.08	–	–
46.1	0.05	0.930	–	–	–	–

Analysis of the intensities of the interference maxima and the values of the interplanar spacings given in Table 1 indicates a comparatively rapid oxidation of the thin neodymium film at room temperature and the formation thereby of the sesquioxide of cubic modification. Investigation of a number of other films, even those formed by evaporation and condensation of neodymium obtained from a 45% magnesium–neodymium alloy after distillation of magnesium from it in high vacuum, also showed that they consist of neodymium and the same sesquioxide.

Electron diffraction investigation of films kept in air for 2 hours (one of them is shown in Fig. 1b) and for 2 days (Fig. 1c) made it possible to establish that

Fig. 1. Electron diffraction patterns of neodymium films: a—evaporated in vacuum; b—the same film after 2 hours of exposure to air at room temperature; c—after 2 days of exposure to air at room temperature; d—after heating at 500° in air; e—after heating at 700° in air; f—after heating at 900° in air; g—sprayed at 1800-1900° in a vacuum of 10^{-8} mm.

Figure 1: Fig. 1. Electron diffraction patterns of neodymium films: a—evaporated in vacuum; b—the same film after 2 hours of exposure to air at room temperature; c—after 2 days of exposure to air at room temperature; d—after heating at 500° in air; e—after heating at 700° in air; f—after heating at 900° in air; g—sprayed at 1800-1900° in a vacuum of 10^{-8} mm.

even at room temperature oxygen diffuses into the film quite intensively. This is indicated, in particular, by the absence in the electron diffraction pattern of Fig. 1b of rings characteristic of neodymium. Calculation of the electron diffraction pattern in Fig. 1b showed that the compound formed has a cubic crystal lattice with a constant $a = 11.21$ Å, i.e., somewhat larger than that indicated in (5) for neodymium sesquioxide of the cubic modification, for which $a = 11.05$ Å.

From the electron diffraction patterns in Fig. 1b,c it is seen that the interference rings from the compound formed are blurred. This circumstance may indicate a strong distortion of its lattice.

Despite the considerable scatter in the values of the lattice constants calculated from individual interference rings in Fig. 1c, the mean value $a = 11.36$ Å indicates a continuing increase in the dimensions of the unit cell of neodymium sesquioxide with increasing duration of its exposure to air at room temperature.

The data obtained and the considerable blurring of the diffraction pattern provide grounds to suppose that under the specified conditions the dissolution (diffusion) of oxygen in the lattice of neodymium sesquioxide continues, as a result of which it (the lattice) is nonuniformly distorted.

Analysis of the intensities of the interference rings and extinctions makes it possible to consider that the lattice of cubic neodymium sesquioxide may be assigned to one of the following space groups: $P23$; $P2_{13}$; $Pm3$; $P\bar{1}3m$; $P\bar{4}3n$; $P43$; $P4_{23}$; $P4_{33}$; $P4_{13}$; $Pm3m$; $Pm\bar{3}n$.

Raising the heating temperature of the neodymium film to 500° leads to a substantial change in its structure. Calculation of the electron diffraction pattern shown in Fig. 1d established that the compound formed also has a cubic lattice with constant $a = 11.05$ Å. With a further increase in the temperature of the specimen (to 700°), the intensities and sharpness of the interference rings increase in the corresponding electron diffraction patterns, indicating an increase in the degree of ordering of atoms in the crystal lattice. The calculation data for the electron diffraction pattern of such a specimen at $2L\lambda = 42.7$ are given in Table 2.

Fig. 1. Electron diffraction patterns of neodymium films: **a**—evaporated in

vacuum; **b**—the same film after 2 hours of exposure to air at room temperature; **c**—after 2 days of exposure to air at room temperature; **d**—after heating at 500° in air; **e**—after heating at 700° in air; **f**—after heating at 900° in air; **g**—sprayed at 1800-1900° in a vacuum of 10^{-8} mm.

The mean value of the lattice constant is $a = 11.05 \pm 0.03$ Å. In accordance with the analysis of extinctions and the indices of the reflecting planes, the compound formed may be assigned to one of the space groups indicated above. The obtained value of the lattice constant of the compound formed in air at 500—700°, despite its containing a larger amount of oxygen than the sesquioxide, nevertheless proved to be the same as that of cubic Nd_2O_3.

Table 2

$2r$	I	d, Å	hkl	a, Å	$2r$	I	d, Å	hkl	a, Å
10.8	0.25	3.91	220	11.06	32.6	0.20	1.31	563	11.12
14.5	1.00	2.94	321	11.00	35.6	0.20	1.19	565	11.05
17.5	0.20	2.44	421	11.08	37.5	0.02	1.139	637	11.05
19.5	0.02	2.18	431 510	11.08	38.7	0.02	1.12	566	11.05
20.08	0.50	2.06	521	11.30	45.7	0.15	0.934	569	11.10
25.0	0.50	1.71	541	11.08	50.5	0.15	0.846	589	11.08
29.1	0.30	1.47	264	11.00					

The reason for this preservation of the volumes of unit cells containing appreciably different amounts of oxygen is explained by the specificity of the oxygen compounds of a number of metals, including rare-earth metals, which form defective structures ([6]).

For an approximate determination of the composition of the compound formed under the indicated conditions, we made estimation calculations. The data obtained indicate that during the heating of the sesquioxide of neodymium of cubic modification, the change in interplanar spacings reaches appreciable values. These changes give corresponding changes in the mean values of the lattice constants.

Some of the data used, necessary for the above-mentioned estimate calculation, are given in Table 3.

Table 3

hkl	d_{initial}	d_{final}	Δd, Å	Δa, Å
222	3.16	3.28	0.12	0.415
400	2.76	2.89	0.13	0.520
440	1.92	1.98	0.06	0.340
622	1.64	1.72	0.08	0.530

The scatter of the values indicated in Table 3 permits the assumption that oxygen atoms are distributed nonuniformly throughout the entire volume of the crystal lattice. For our further calculations we use the mean value of the changes in the lattice constant, Δa, equal to 0.451 Å.

Since the diameter of an oxygen atom is 1.32 Å, then, without taking into account the phenomena of polarizability, compression, etc., which affect the dimensions and state of the oxygen atoms introduced into the oxide lattice, we shall determine the fraction of introduced oxygen per one unit cell of the oxide, assuming that it has a close packing of atoms.

In the initial cell of Nb_2O_3, each neodymium atom corresponds to 1.5 oxygen atoms. Proceeding from the linear changes of the lattice of this compound (which is not entirely correct), the limiting amount of introduced oxygen (according to the electron-diffraction measurement data) is equal to

$$\frac{\Delta a_{\text{av}}}{2r_{\text{at O}_2}} = \frac{0.45}{1.32} \sim 0.34$$

atom per one unit cell of Nb_2O_3.

Thus, at the maximum saturation of neodymium sesquioxide with additionally introduced oxygen at 700°, each neodymium atom corresponds to 1.84 oxygen atoms. Recalculation of the gross amount of oxygen to neodymium atoms gives grounds to believe that this amount

neodymium and oxygen corresponds to the compound Nd_6O_{11}. This result is confirmed by weighing the neodymium film before and after oxidation.

The new compound observed by us at 500° apparently has a composition corresponding to the formula Nb_6O_{11}. Its lattice is cubic, with the constant

$$a = 11.05 \pm 0.03 \text{ Å}.$$

Examination of the film heated at 900° indicates a further change in the diffraction pattern. Calculation of the electron diffraction pattern shown in Fig. 1e established the presence in it, along with several weakened rings corresponding to the presumed compound Nd_6O_{11}, also of additional ones. The latter may arise either from the formation of a new phase with the constant $a = 11.05$ Å, or from distortion of the crystal lattice of the indicated compound, as a result of which, instead of cubic, it becomes tetragonal, with the ratio of axes c/a close to 1. Such a distortion of the crystal lattice is quite probable, according to Mikheev' s scheme of structural reversibility under deformations (7).

When the heating temperature of the film was raised above 900°, the copper grids became fragile and it was not possible to prepare specimens for study. In addition to the films mentioned, a film formed after the evaporation of neodymium at temperatures of 1800–1900°, in a vacuum equal to 10^{-3} mm Hg, was also studied by the electron diffraction method. The electron diffraction pattern of such a film is shown in Fig. 1 . The mean value of the lattice constant calculated from this electron diffraction pattern is 11.24 ± 0.03 Å.

The obtained value of the lattice constant of the compound formed proved to be close to that known from the literature (8) for cerium dioxide (CeO_2). This circumstance makes it possible to suppose that, under the indicated conditions, the compound NdO_2 was probably formed, about whose existence nothing is yet known.

Thus, investigation of the oxidation process of neodymium in the form of a thin film in air showed that at temperatures up to 700° Nd_2O_3 and, probably, Nd_6O_{11} are formed. The compound apparently corresponding to NdO_2 was obtained only upon oxidation of neodymium vapor. All these compounds have a cubic crystal lattice.

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REFERENCES CITED

1. D. Yost, G. Russell, K. Garner, *The Rare Earth Elements and Their Compounds*, 1949.
2. O. N. Morozov, *Chemistry of the Rare Elements*, 1938.
3. R. C. Vickery, Ind. Chem. and Chem. Manufact., **29**, 260 (1953).
4. L. K. Frevel, Ind. and Eng. Chem. Anal., **14**, No. 9 (1942).
5. L. K. Frevel, H. W. Rinn, Anal. Chem., **25**, No. 11 (1957).
6. F. Trombe, Bull. Soc. Chim. France, No. 10, 1010 (1953).
7. V. I. Mikheev, *X-ray Determinative Guide to Minerals*, Moscow, 1957.
8. T. Moeller, Rec. Chem. Progr., **14** (2), 69 (1953).
9. W. F. Meggers, Science, **105**, 514 (1947).

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