# Reports of the Academy of Sciences of the USSR

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1965

SovietRxiv

## Abstract

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Reports of the Academy of Sciences of the USSR

1965. Volume 161, No. 3

Chemistry

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# On the Nature of Irreversible Polymorphic Transformations of Rare-Earth Oxides

*(Presented by Academician N. P. Sazhin on 9 X 1964)*

Irreversible, so-called monotropic, polymorphic transformations are known for many inorganic substances and compounds. Elucidating the nature of irreversible transformations is of theoretical and practical interest for a number of problems in the physics and chemistry of the solid state and, apparently above all, for work on the synthesis of new substances at high and ultrahigh pressures.

Polymorphic transformations observed in a number of rare-earth sesquioxides: $Pr_2O_3$, $Nd_2O_3$, $Sm_2O_3$, $Gd_2O_3$, etc., are of particular interest for studying the nature of polymorphism, since the corresponding polymorphic forms of the oxides, A, B, and C (according to Goldschmidt' s classification), are completely isomorphous with one another, and their lattice parameters change in proportion to the cation radii in this series of oxides. Transformations of rare-earth oxides are interpreted in most cases by Goldschmidt ([1]), Shafer and Roy ([2]), and Warshaw and Roy ([3]) as reversible. In other works ([4], [5]), however, it has been shown that the polymorphic transformations, at least for the oxides of neodymium, samarium, europium, and gadolinium, are irreversible.

In practically all investigations devoted to the study of the polymorphism of rare-earth-element oxides, X-ray determinations were carried out only for quenched specimens at room temperature, which made it difficult to establish the possibility of reversible transformations, if they existed. The authors of work ([5]), it is true, carried out high-temperature X-ray studies of Nd, Sm, Eu, and Gd oxides, but only up to temperatures of the order of 1500°. Therefore the question of the actual existence of high-temperature polymorphic transformations, for example for the oxides of terbium and dysprosium, concerning which there are only indirect indications in the literature ([1], [3]), as well as of possible high-temperature transformations of other oxides, could be resolved only by direct X-ray investigations at temperatures up to 2200–2300°. Such investigations were carried out

Figure 1 and Figure 2

Figure 1: Figure 1 and Figure 2

by us in a special high-temperature vacuum X-ray camera for the oxides Pr, Nd, Sm, Gd, Tb, and Dy.

In parallel with the vacuum X-ray measurements, weight losses in the temperature range of the transformation were also investigated; the influence on the transformation temperature of the gaseous medium in which the experiment was conducted (oxidizing, reducing, vacuum) and of pressure was studied; and chemical analysis was performed for the content of "excess"(above the 2:3 composition) oxygen by the iodometric method. The starting preparations used were: $Pr_6O_{11}$ "Pr-1" (99.5%); $Nd_2O_3$ "N-1" 99.5%; $Sm_2O_3$ "Sm-1" 99.9%; $Gd_2O_3$ "Gd-1" 99.5%; $Tb_4O_7$ "Tb-1" 99.9%; $Dy_2O_3$ "Di-1" 99.9%.

According to the data of Wicker ($^6$), Gatta, Iring, and others ($^7$), the polymorphic transformation C → A of praseodymium oxide (from the cubic to the hexagonal modification) occurs within the limits of the sesquioxide composition. Taking into account the known property of oxygen-rich phases of praseodymium oxide to be reduced in the temperature range close to the transformation temperature, the reduction process ⋯

reduction was studied during heating in vacuum by gravimetric and iodometric methods, as well as by measurements of the lattice parameter up to the transition temperatures. In order to completely eliminate the influence of possible contamination of the industrial praseodymium oxide by products of reaction with carbon dioxide, nitrogen, or water, the starting preparation was reduced in a vacuum of the order of $1 \cdot 10^{-5}$ mm Hg at 1100° to $Pr_2O_3$, and was then oxidized in carefully dried hydrochloric acid purified from hydrogen ($p = 600$ mm Hg) for 25 h at temperatures of 1100—100°

**Fig. 1.** Dependence of the lattice parameters and the content of "excess"oxygen on temperature for the oxides of praseodymium, terbium, and dysprosium.
*a*—$PrO_x$, *b*—$Pr_2O_3$, *v*—$TbO_x$, *g*—$Tb_2O_3$, *d*—$Dy_2O_3$, *e*—percentage of "excess" oxygen for $PrO_x$, *zh*—the same for $TbO_x$.

**Fig. 2.** Dependence of transformation temperatures for the oxides of praseodymium, neodymium, and samarium in different media.
1*a*—$Nd_2O_3$—air, 1*b*—$Nd_2O_3$—vacuum $1 \cdot 10^{-5}$ mm Hg, 1*v*—$Nd_2O_3$—hydrogen 130 kg/cm$^2$, 2*a*—$PrO_x$—air, 2*b*—$PrO_x$—argon 5 kg/cm$^2$, 2*v*—$PrO_x$—hydrogen 130 kg/cm$^2$, 3*a*—$Sm_2O_3$—air, 3*b*—$Sm_2O_3$—hydrogen 130 kg/cm$^2$.

(filters: 1) "hot" 800°—filter with platinized corundum, 2) multistage filter with phosphorus pentoxide, 3) filter with corundum powder at −70°).

As a result of such treatment, an oxide of composition $PrO_2$ was obtained with an accuracy, in oxygen by weight, of up to ±0.02%, which in itself is of considerable interest. The change in the parameter of the cubic cell of $PrO_2$ as

Fig. 3. X-ray diffraction patterns of the C- and B-forms of terbium oxide at various temperatures. a –B-form, room temperature (quenched from 2000°); b –C-form, 1000° (slow cooling from 2020°); c –C-form, 1850°

Figure 2: Fig. 3. X-ray diffraction patterns of the C- and B-forms of terbium oxide at various temperatures. a –B-form, room temperature (quenched from 2000°); b –C-form, 1000° (slow cooling from 2020°); c –C-form, 1850°

it is reduced to $Pr_2O_3$ is shown in Fig. 1. It should be noted that all X-ray diffraction patterns were indexed with a sufficient degree of accuracy in the cubic system with a cell doubled relative to that of $PrO_2$. The cell parameter of the initial $PrO_2$ was 5.391 Å. The data on the content of "excess" oxygen shown in the same figure indicate that the processes of reduction and of the polymorphic transformation from the C- to the A-form overlap one another. In direct connection with this, experiments were carried out on the reduction of $PrO_2$ and determination of the $C \rightarrow A$ transition temperature at an elevated hydrogen pressure of 130 $kg/cm^2$. With the aid of high-temperature X-ray photographs in air, the transformation temperature in an oxidizing medium was likewise determined (Fig. 2). It is evident from the figure that the $C \rightarrow A$ transformation temperature for praseodymium oxide varies within the range from 700 to 1350°, depending on the nature of the medium; thus it is obvious that the change in structure for oxide compositions close to sesquioxides is directly connected not only with thermodynamic conditions, but equally with a change in the composition of the compound. In this sense, the $C \rightarrow A$ transformation of praseodymium oxide, strictly speaking, cannot be regarded as a true polymorphic transformation. Within the framework of the observed phenomenon, the irreversibility of the transformation in experiments in vacuum or in an inert medium is readily explained, since even insignificant oxygen losses cannot be compensated in the course of the reverse transition. Fig. 2 also shows data for transition temperatures in different media for $Nd_2O_3$ and $Sm_2O_3$. As follows from the figure, the transition temperatures for these

oxides also decrease considerably (by $\sim 100°$) for experiments in hydrogen, as compared with experiments in air and argon. Weight measurements for $Nd_2O_3$, $Sm_2O_3$, and $Gd_2O_3$ established small but noticeable mass losses ($0.04 \leq \Delta \leq 0.1\%$) in the temperature ranges corresponding to the $C \rightarrow A$ and $C \rightarrow B$ transformations. Oxygen analysis for the C-forms of these oxides showed that their composition, to within ±0.02% in oxygen content,

**Fig. 3.** X-ray diffraction patterns of the C- and B-forms of terbium oxide at various temperatures. *a* –B-form, room temperature (quenched from 2000°); *b* –C-form, 1000° (slow cooling from 2020°); *c* –C-form, 1850°.

corresponds to the sesquioxide. Therefore, taking into account the results of experiments in a reducing atmosphere and of weighing, it may be supposed that the transitions from the C-form to the A- and B-forms for the oxides $Nd_2O_3$, $Sm_2O_3$, and $Gd_2O_3$ are associated with their partial reduction to a composition somewhat deficient in oxygen relative to the sesquioxide; however, this consideration requires additional special verification. The irreversible character of the transformations in the oxides is definitely associated with the observed mass losses, which is indirectly confirmed by the results of experiments obtained for the oxides of terbium and dysprosium.

High-temperature X-ray investigation of the A- and B-forms of the sesquioxides Pr, Nd, Sm, and Gd revealed no additional structural changes up to the melting temperatures. The data of X-ray and chemical analyses characterizing the process of reduction of $Tb_4O_7$ to $Tb_2O_3$ are presented in Fig. 1. It is seen from the figure that the reduction of terbium oxide in vacuum is practically completed at a temperature of about 770°.

In X-ray studies of the oxides of terbium and dysprosium in a vacuum of $1 \cdot 10^{-5}$ mm Hg in the temperature region above 1700°, a result unexpected at first glance was obtained: the transformations from the C-form to the B-form proved to be completely reversible for $Tb_2O_3$ (1850°) and for $Dy_2O_3$ (2150°).

The hysteresis of the transformations upon cooling at a rate of 100°/h was, respectively, 300 and 200°. We find the following explanation for this fact: by virtue of crystal-chemical causes (the rather small radii of the cations), the stability region of the C forms of Tb and Dy oxides extends to very high temperatures, as a result of which the substantial changes in composition during heating are completed before the boundary of the region of existence of the C form is reached. Therefore, if changes in composition do occur during the transition, they are very small and can be restored through disproportionation upon a sufficient lowering of the temperature and transition into the stability region of the C form. Under rapid cooling ($> 150°$/s), the B form of $Tb_2O_3$ can be quenched, whereas B-$Dy_2O_3$ is not quenched even under these conditions. X-ray diffraction patterns of the C and B forms of $Tb_2O_3$, obtained at different temperatures, are shown in Fig. 3. In order to determine whether the restoration of the C forms of $Tb_2O_3$ and $Dy_2O_3$ upon cooling of the corresponding B forms was connected with contamination in the chamber at very high temperatures, additional experiments were carried out in an electron-beam apparatus. Samples of terbium and dysprosium sesquioxides pressed in the form of small cylinders were melted under special conditions by an electron beam, so that in the high-temperature zone the sample did not come into contact with parts of the apparatus and, moreover, the possibility of contamination of the sample due to evaporation of the heated fittings was eliminated. The samples were then cooled at a rate of 100°/s; the molten core was prepared and X-rayed at room temperature. For both $Tb_2O_3$ and $Dy_2O_3$, only the low-temperature C modifications were obtained.

Thus, the clearly reversible character of the observed transformations for terbium and dysprosium oxides, and the irreversible character for praseodymium, neodymium, samarium, and gadolinium oxides, have a common basis associated with subtle changes in composition occurring in the rare-earth oxides in the transition region during heating.

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Received1 X 1964

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