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ON THE PRODUCTION OF SINGLE CRYSTALS OF OXIDES OF RARE-EARTH ELEMENTS BY THE VERNEUIL METHOD

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It is known that under certain conditions some lanthanides are capable not only of forming sesquioxides, but also of passing into lower and higher oxidation states (^1). It is also known that in the Verneuil method even slight changes in the composition of the flame are sometimes accompanied, following a change in the oxidation–reduction potential of the crystallization medium, by the appearance and growth of crystals of an undesirable composition. In this connection it seemed expedient, along with repeating (2-5) and continuing (^6) investigations on the study of the conditions for growing single crystals of oxides of rare earths present in the trivalent state, to reveal the possibilities of the Verneuil method for obtaining oxides containing the indicated elements in another valence state, and then to establish the permissible limits of variation of the gas regimes for crystallization of one or another composition.

The experiments were carried out with oxides of lanthanides of atomic numbers from 62 to 71. Among the elements of the series investigated, four—samarium, europium, terbium, and ytterbium—possess variable valence. When they were used, primary attention was paid to the composition of the flame, in particular to the ratio of the volumes of hydrogen and oxygen entering the burner, with the value H_2/O_2 being taken as a conditional characteristic of the medium in the crystallization space of the furnace (^7, ^8). Spontaneous formation and subsequent growth of crystals were carried out in a conventional apparatus equipped with a two-tube burner. Cooling of the specimens was achieved by quenching them; if, however, the experiment assumed the possibility of formation of a suboxide form or dioxide of the lanthanide under investigation, the crystal was cooled in a stream of hydrogen or oxygen, respectively.

Specimens grown in the form of single crystals were tested for microhardness; in each case the plane tested was ground parallel to the growth direction, without regard to crystallographic orientation.

The crystallization conditions and the results obtained are summarized in Table 1*. Comparison of the data presented makes it possible to draw the following

conclusions.

1. All the rare-earth oxides investigated, with the exception of terbium, irrespective of the oxidation–reduction potential of the medium in the crystallization space, acquire the trivalent state when crystals are grown by the Verneuil method. X-ray analysis of crystals grown in a reducing medium not only did not show the presence of suboxide forms as the principal phases but, within the sensitivity limits of the method, did not reveal even their traces. This experimental fact indicates the possibility of freely varying the conditions of the gas regime during growth and cooling of the crystals and thereby considerably simplifies control over the course of crystallization of both pure rare-earth oxides and those activated by elements of this series.

* The structural modification was established by the powder method on a URS-50IM; microhardness was determined on a PMT-3 under loads of 50 and 100 g.

Table 1

Substance	Structural modification of powder	Flame composition, H_2 : O_2 by volume	Cooling method	Structural modification of crystal	Crystal color	Microhardness, kg/mm^2
Sm_2O_3	Monoclinic	2.5 : 1	Quenching	Single crystal, monoclinic	Yellow-orange	439
Sm_2O_3	Monoclinic	6.0 : 1	Cooling in H_2	Single crystal, monoclinic	Yellow-orange	439
Eu_2O_3	Monoclinic	2.7 : 1	Quenching	Crystalline intergrowths, monoclinic	Brown	Not determined
Eu_2O_3	Cubic	7.5 : 1	Cooling in H_2	Crystalline intergrowths, monoclinic	Brown	Not determined
Gd_2O_3	Predominantly cubic	3.6 : 1	Quenching	Same	Colorless	Same

Substance	Structural modification of powder	Flame composition, H_2 : O_2 by volume	Cooling method	Structural modification of crystal	Crystal color	Microhardness, kg/mm^2
Dy_2O_3	Cubic	3.6 : 1	Quenching	Single crystal, cubic	Yellow-brown	892
Ho_2O_3	Cubic	3.6 : 1	Quenching	Same	Tobacco-colored	636
Er_2O_3	Cubic	3.6 : 1	Quenching	Same	Lilac-pink	699
Tu_2O_3	Cubic	3.6 : 1	Quenching	Same	Greenish	721
Yb_2O_3	Cubic	3.6 : 1	Quenching	Same	Colorless	733
Yb_2O_3	Cubic	7.5 : 1	Cooling in H_2	Same	Colorless	733
Lu_2O_3	Cubic	3.6 : 1	Quenching	Same	Colorless	832

2. The crystals of the sesquioxides of the lanthanide series studied, obtained by the Verneuil method, belong to different structural modifications: Sm_2O_3, Eu_2O_3, and Gd_2O_3 are monoclinic (B-type), while Dy_2O_3, Ho_2O_3, Er_2O_3, Tu_2O_3, Yb_2O_3, and Lu_2O_3 are cubic (C-type).

It should be noted that, in attempting to grow terbium oxide crystals at an H_2 : O_2 ratio of 3.2 : 1, followed by rapid cooling, the specimen disintegrated within several seconds after removal from the furnace, forming a very fine dust-like mass. X-ray analysis of the latter indicated the presence of an oxide of indefinite composition. Crystallization under a somewhat more oxidizing regime—at H_2 : O_2 = 2.8 : 1—led to the formation of a boule which, as a result of cooling in a stream of oxygen, retained its external shape and color (brownish-black); however, its composition also proved to be indefinite, although different from the preceding one. A still closer approach of H_2 : O_2, with simultaneous melting of the top of the polycrystalline pedestal, proved impossible under the given apparatus conditions.

3. The microhardness of the crystals studied increases with increasing atomic number in the Mendeleev table. The exception is Dy_2O_3, whose comparatively high hardness is probably associated with the presence of impurities of non-lanthanide-group elements.

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