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RARE EARTH SUBOXIDES

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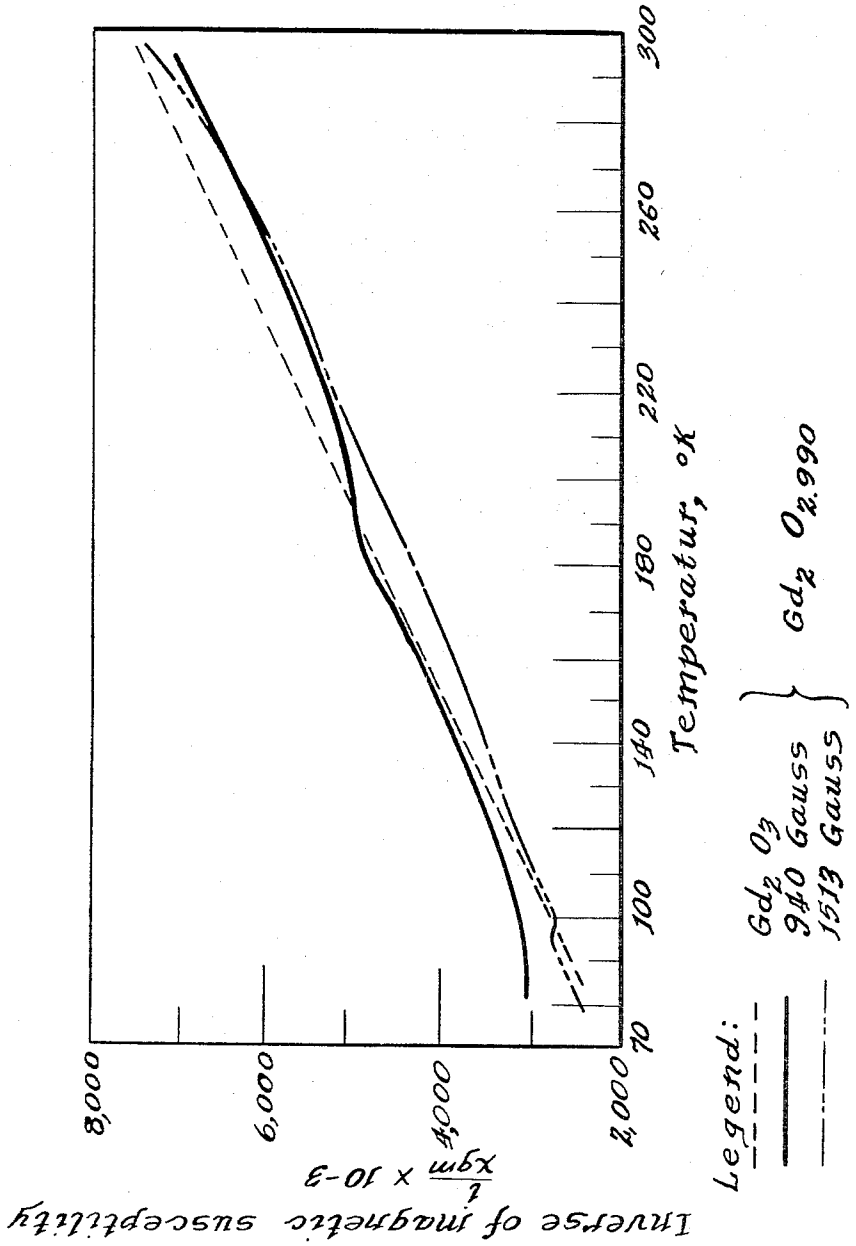

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RARE EARTH SUBOXIDES

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Continuation-in-part of application Ser. No. 339,045, Jan. 20, 1964. This application Nov. 9, 1965, Ser. No. 506,913

2 Claims. (Cl. 23—183)

ABSTRACT OF THE DISCLOSURE

Rare earth suboxides of lanthanum, praseodymium, promethium, yttrium, gadolinium, dysprosium, holmium, erbium and lutetium having the formula Re_2O_x where RE is rare earth and where $2.900<x<3.00$.

The invention described herein was made in the course of, or under, a contract with the U.S. Atomic Energy Commission.

This is a continuation-in-part of application S.N. 339,045, filed Jan. 20, 1964 and now abandoned.

This invention deals with rare earth suboxides, which are oxides that have a lower oxygen content than the normal sesquioxides.

It is an object of this invention to provide rare-earth suboxides that are intensely colored, which is in contradistinction to the normal stoichiomertric sesquioxides, which are pale, light-colored or even white. These substoichiometric rare-earth oxides also possess enhanced magnetic susceptibilty and electrical conductivity compared to the normal stoichiometric sesquioxides of the rare earths.

It has been found, surprisingly, that rare earth oxides whose oxygen content is lower than corresponds to stoichiometric sesquioxides have radically different characteristics than the latter. Both the stoichiometric and nonstoichiometric rare-earth oxides are semiconductors under the scientific definition of such. However, the suboxides appear to have a higher conductivity than the stoichiometric variety. For instance, while lutetium sesquioxide, Lu_2O_3, is white and diamagnetic, lutetium suboxide is deep violet and paramagnetic. These findings have been observed on yttrium oxide and also on lanthanum, praseodymium, promethium, gadolinium, dysprosium, holmium, erbium, and lutetium oxides. The formula of the suboxides was determined to be RE_2O_x where

$$2.900<x<3.000$$

(RE is used as the general symbol for rare earth).

The crystal structure of the suboxide was found to be the same as that of the stoichiometric sesquioxides. For most of the rare earths the crystal structure of the oxides is cubic. As mentioned, the electrical resistivity is rather high for the suboxides; however, the conductivity can be increased by the incorporation of conducting metals, such as silver or copper. This incorporation can be combined with the production of the suboxides. For instance, an oxalate of silver or copper can be mixed with the starting rare earth compounds and processed with the rare earth compounds for the manufacture of the suboxides.

The suboxides can be prepared by various methods known to those skilled in the art, which broadly is by partial decomposition of the higher stoichiometric oxides in a high vacuum or in a reducing atmosphere at elevated temperature. For instance, the sesquioxides can be subjected to such partial decomposition in a vacuum of about 5×10^{-6} Torr at elevated temperature using the floating-zone technique. Another means of preparing the suboxide is by arc-melting of a mixture of the sesquioxide and a metal; the metal can either be the same rare earth as that of the suboxide to be prepared, or another rare earth, or even a foreign metal such as iron, copper or nickel. Instead of arc-melting, the mixture can also be heated in a furnace to from 2250 to 2500° C. In either instance the excess metal is then dissolved by means of an acid such as hydrochloric acid.

Still another method is the vacuum-heating of a compacted rare earth sesquioxide-hydride mixture at about 800° C. for the decomposition of the hydride and removal of the hydrogen followed by heating to about 2000° C. in an inert atmosphere, for instance in argon. Finally, the rare earth metal oxalate can also be mixed with another rare earth or foreign oxalate; the mixture is then dried at about 200° C. in a helium atmosphere, heated to 300° C. in helium and finally in hydrogen at about 1400° C. These processes of preparing the suboxide, although new as applied to the rare earth suboxides, are not being claimed as part of the invention.

The suboxides, on acount of their outstanding characteristics, have various types of utility. For instance, they can be used in the microwave field and for magnetic cores. They also can serve as semiconductors, as thermoelectric generators, and as elements in lasers.

The attached drawing shows three diagrams, two made with gadolinium suboxide of the formula $Gd_2O_{2.990}$ at two different magnetic intensities and one with stoichiometric gadolinium sesquioxide, Gd_2O_3. On the ordinate the inverse value of the magnetic susceptibility is plotted, while on the abscissa the respective temperatures are entered in degrees K. It will be noticed from that drawing that below 180° K. the stoichiometric gadolinium oxide has a higher magnetic susceptibility than the suboxide but that above about 180° K. the suboxide has a higher magnetic susceptibility than the stoichiometric Gd_2O_3.

In the table below electrical resistivity values of some suboxides are compared with those of the corresponding sesquioxides. In all cases the suboxides have considerably lower values than the sesquioxides.

Oxide:	Resistivity at 298° K., ohm-cm.
Gd_2O_3	4×10^5
$Gd_2O_{2.990}$	8×10^2
Er_2O_3	6×10^4
$Er_2O_{2.978}$	1×10^3
Ho_2O_3	8×10^4
$Ho_2O_{2.980}$	1×10^3
Lu_2O_3	3×10^4
$Lu_2O_{2.970}$	6×10^2
Y_2O_3	5×10^4
$Y_2O_{2.982}$	6×10^2

It will be understood that the invention is not to be limited to the details given herein but that it may be modified within the scope of the appended claims.

The embodiments of the invention in which an ex-

clusive property or privilege is claimed are defined as follows:

1. A suboxide of the rare earth lanthanum, praseodymium, promethium, yttrium, gadolinium, dysprosium, holmium, erbium or lutetium having the formula Re_2O_x where $2.900<x<3.000$ and where RE is the rare earth.

2. Yttrium suboxide of the formula $Y_2O_{2.982}$.

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