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Thermal Emission, Electrical Conductivity, and Hall Effect for Defects Study at High Temperature ($T \geqslant 1250°K$) in Refractory Oxides (Y_2O_3, TiO_2)

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It is shown that information on atomic point defects in oxides, at high temperature, may be obtained from a study of thermal emission of electrons. A simple dependence of emission against oxygen pressure is observed for Y_2O_3 and TiO_2 compounds. It is stated that this new experimental method depends only on the electron concentration and not on other carriers, as electrical conductivity does.

Electrical conductivity data of single crystals of TiO_2 (rutile) in large oxygen pressure and temperature ranges are rationalized in terms of a defect model involving ionized titanium interstitials. Preliminary results concerning Hall effect on this material are presented.

Introduction

At high temperature, more or less important deviations from stoichiometry may occur in refractory oxides. For small deviations, a model of single point defects is the most currently suggested (*1*). A comprehensive study of nonstoichiometry implies the identification of main defects, the measurement of their concentration or its variation with oxygen pressure; then one must explain their influence on physical properties. Two kinds of experiments are generally used: gravimetry (*2*) and electrical conductivity (*3*) as a function of oxygen pressure. The first one is a direct way to follow defect concentration, but it is difficult to achieve at high temperature when thermal disorder and weight changes are small (*2*). Certain precautions must be taken in the collection and interpretation of the data of the second one, each carrier in a mixed conductor having its own mobility (*3*).

A new method, first investigated in our laboratory by Loup (*4*), is based on thermal emission of electrons, which enables us to follow concentration of electrons as a function of oxygen pressure. We briefly outline thermal emission theory, then we describe results obtained on Y_2O_3 and TiO_2 in terms of point defects associated with the bulk. We also present some results obtained by means of electrical conductivity on TiO_2 (rutile).

I. Theory of Thermal Emission of Electrons

The density of emitted current for a solid heated at a temperature T is given by the Richardson's law:

$$J_0 = AT^2 \exp(-\Phi/kT). \qquad (1)$$

J_0 is the density of emitted current, extrapolated to a null tension between anode and cathode, according to the Schottky law. Φ is the work function, i.e., the difference between electron energy in vacuum and Fermi energy.

For a nondegenerated semiconductor, this law becomes (*4*):

$$J_0 = BT^{1/2} n \exp(-\chi/kT). \qquad (2)$$

n is the concentration of electrons in the conduction band; χ is the external work function, i.e., the difference between electron energy in vacuum and the energy at the bottom of the conduction band.

Thermal emission, as electronic conductivity $\sigma_e = (n_n^{\mu} + p_p^{\mu})e$ is simply related to the carrier concentration, and one may easily compare the two kinds of measurements.

II. The Thermal Emission of Electrons, a Means of Investigation of Point Defects

For an oxide in thermodynamic equilibrium with the surrounding gas phase, one may more or less change the native disorder by imposing variations of oxygen activity in the gas phase. In the framework of point defects model, one may follow the deviation from stoichiometry by means of carrier concentration.

We now employ the well known formalism of Kröger and Vink (*5*). Let us imagine, for instance, that an oxygen leaves its normal site O_O^x, thus generating an oxygen vacancy $V_O^{2\cdot}$:

$$O_O^x = 1/2\ O_2(g.) + V_O^{2\cdot} + 2e. \qquad (3)$$

If the vacancies are the predominant defects, the concentration of electrons, at a fixed temperature, obeys to the law:

$$n \propto p_{O_2}^{-1/x} \qquad x = 6 \qquad (4)$$

and after Eq. (2):

$$\log J_0 = C^{st} - 1/x \log p_{O_2}. \qquad (5)$$

According to the type of defect involved in the oxide, and with simplified electroneutrality equations, one may carry out isotherms of defects concentration as a function of oxygen pressure. For instance, in Fig. 1, in the case of a Frenkel disorder, relative to oxygen (oxygen vacancies and oxygen interstitials), are shown isotherms of defects concentration. According to the relative importance of the two kinds of defects, three distinct pressure ranges appear. Each domain is governed by a different electroneutrality equation. Interpretation of the results of thermal emission is then easy, since changes in thermal emission reflect changes in electronic concentration. We now corroborate such a theory on two examples.

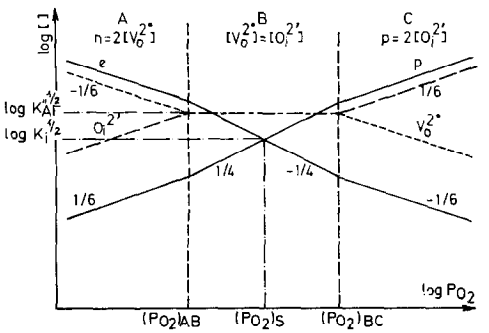

FIG. 1. Anti-Frenkel disorder. Isotherms of point defects concentration.

On Fig. 2, emission isotherms for yttrium oxide Y_2O_3 are plotted as a function of oxygen pressure at several temperatures. A linear variation, in agreement with Eq. (4) is found with $x = 4$ in a great part of the pressure range. This slope indicates for Y_2O_3 an anti-Frenkel disorder (oxygen vacancies $V_O^{2\cdot}$ and oxygen interstitials $O_i^{2'}$) (*6*). To that kind of disorder, corresponds the diagram of point defects we displayed previously in Fig. 1.

On Fig. 3 are plotted results which have been just obtained in our laboratory, for TiO_2. The emission power for electrons is very small with regard to that of Y_2O_3. So study of emission of the metallic wire is needed and it is compared with that of TiO_2 in Fig. 3. It is seen that its influence on the linear dependence of $\log J_0$ against $\log p_{O_2}$ is negligible and that Eq. (4) is correctly followed in the studied range. Other experiments are still in progress.

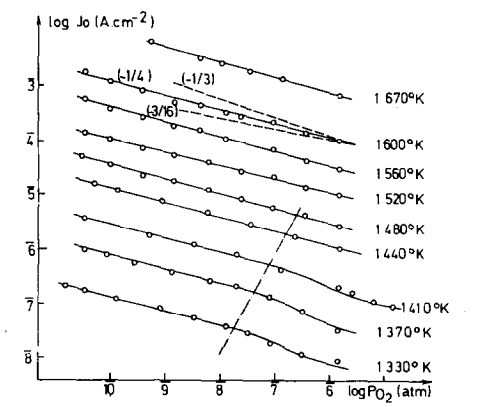

FIG. 2. Emission isotherms for yttrium oxide Y_2O_3.

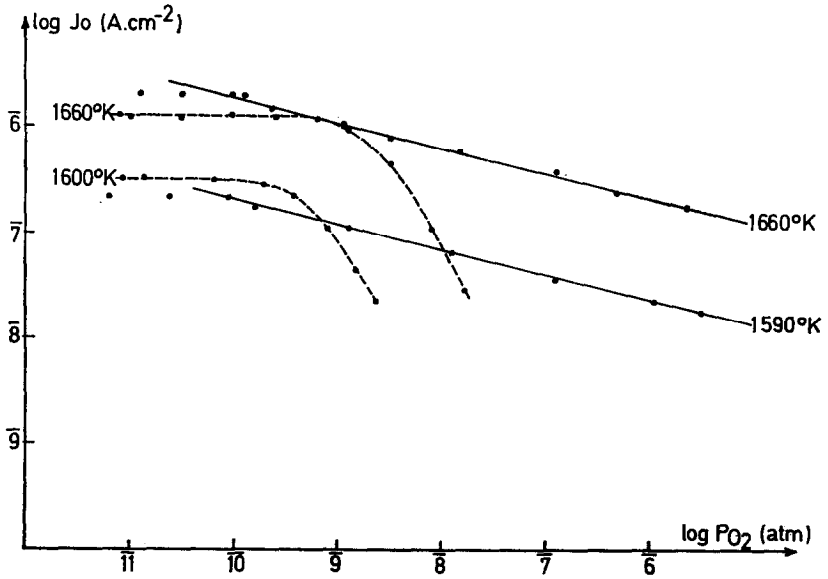

FIG. 3. Emission isotherms for titanium dioxide TiO_2 and rhodium. ○ : TiO_2 on Rh; ● : pure Rh.

So, thermal emission may be considered as a complementary means of investigation of point defects to electrical conductivity and gravimetry. In the case of Y_2O_3 the conclusions we came to are in agreement with previous results of conductivity of Tallan and Vest (*8*), and Robert (*9*). At higher oxygen pressures, data obtained by Robert (*9*) define $a + 1/6$ slope and *p*-type conductivity attributed by us to ionized oxygen–oxygen interstitials. In the same way, data of Tallan and Vest (*8*) in a larger oxygen pressure range may well be interpreted by use of three electroneutrality equations.

High vacuum system is necessary for thermal emission, so very clean technique is used, avoiding carbon contamination for instance. Numerous investigators (*3*) pointed out the influence of impurities, in the pressure range where the material is nearly stoichiometric, as soon as the concentration of thermal defects is below, let us say, 100 ppm. In an oven with alumina tube it is quite difficult to avoid such a contamination.

On the other hand, the heating of a very pure metallic wire, coated with oxide by Joule effect shortens contamination within the experimental process and ensures a good reliability of the results.

III. Electrical Conductivity of Titanium Dioxide TiO_2

We reinvestigated electrical conductivity of titanium dioxide in a large range of oxygen pressure and temperature, where this oxide is stable. Conductivity isotherms were obtained on monocrystalline disks, the geometrical axis of which was parallel to the crystallographic axis, by the method of Vander Pauw (*10*). Several oxygen partial pressures were carried out by gas mixtures O_2–Ar and CO–CO_2, according to a very classical method (*3*).

The slopes of conductivity isotherms (Fig. 4) are all near $-1/5$, in the greatest part of the domain, at the lower oxygen pressures. Neither change in the slope of the isotherms, nor curvature is observed at intermediate pressures, in opposition with previous studies (*11*). So, we may reasonably assume that a single type of defect, titanium interstitials is necessary to the interpretation:

$$Ti_{Ti}^{x} + 2O_O^{x} = Ti_i^{4\cdot} + 4e- + 1/2\ O_2(g.).$$

At higher oxygen pressures, however ($p_{O_2} \geqslant 10^{-3}$ atm) the electrical conductivity does not follow the same law. Extrapolation

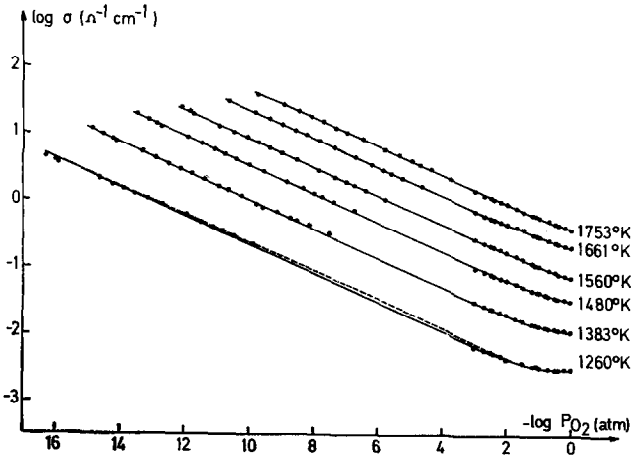

FIG. 4. Electrical conductivity isotherms for TiO_2. ----: Calculated curve at $T = 1260°K$.

of gravimetry data at low oxygen pressures suggests a defect concentration in pure rutile of order of 10 ppm, under pure oxygen. Single crystals never present such a high purity. We have then tested another electroneutrality equation:

$$n + [F'_{Ti}] = p + 2[V_O^{2\cdot}] \qquad (6)$$

where $[F'_{Ti}]$ denotes the concentration of a trivalent impurity in substitution on a normal site Ti_{Ti}^{x}. We then adjusted at 1260°K the theoretical curve to experimental data. We suppose that electron and hole mobility are the same and equal to 0.17 cm^{-2} V^{-1} sec^{-1}, as we found by combining electrical conductivity and gravimetry (*12*) data at $p_{O_2} = 10^{-10}$ atm. An impurity concentration of the order of 30 ppm is found and a good agreement is observed between experimental data and theoretical curve, as is shown in Fig. 5. So, conductivity measurements in air, as a function of temperature, for titanium dioxide, are meaningless, since in this range of oxygen pressure, conductivity is controlled by impurities rather than by intrinsic properties of the material itself.

We also attempted to obtain data on electron and hole mobility by Hall effect. A double ac technique was used to avoid problems associated with high temperature apparatus. At 1300°K, the hole Hall mobility seems to be of the order of 10^{-1} cm^2 V^{-1} sec^{-1} and it decreases rapidly from $p_{O_2} = 1$ atm to $p_{O_2} = 10^{-3}$ atm. The electron Hall mobility is until now below the sensitivity limit of our apparatus. Its value is below or of the order of 10^{-2} cm^2 V^{-1} sec^{-1}. Experiments are in progress to obtain its exact value.

Conclusion

Thermal emission of electrons appears to be a powerful technique for investigation of point defects in oxides at high temperature. It may be associated with other techniques as gravimetry and electrical conductivity. One great advantage is to take electron concentration only into account, while electrical conductivity is governed by the concentration of all mobile carriers, and by their mobilities.

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