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ELECTRONIC CONDUCTION IN PURE AND CHROMIUM-DOPED RUTILE AT 1273 K

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Résumé - La chaîne symétrique Pt-TiO₂-Pt a été étudiée par spectroscopie d'impédance complexe à T = 1273 K dans le cas du rutile pur et dopé au chrome dans le domaine des pressions partielles d'oxygène comprises entre 10⁻¹² et 1 atm. Les variations isothermes de la conductivité électronique du rutile dopé avec 1 à 5 % d'atomes de chrome en fonction de la P₀₂ ont été interprétées dans le cadre de la théorie des défauts ponctuels par le modèle du chrome à valence variable.

L'étude comparative du rutile pur et dopé permet notamment de déterminer les constantes d'équilibre de création des différents défauts, la mobilité des électrons, la largeur de bande interdite et l'énergie d'ionisation du chrome accepteur.

Abstract - The symmetric chain Pt-TiO₂-Pt was studied by means of complex impedance spectroscopy at T = 1273 K for pure and chromium-doped rutile in the partial pressure of oxygen range from 10⁻¹² to 1 atm.

The isothermal variations of electronic conductivity of rutile doped with 1 to 5 % atoms Cr as a function of P₀₂ were interpreted in terms of point defects by the model of mixed-valence chromium.

The comparative study of pure and doped rutile permits us more particularly to determine the different defect equilibria constants, the electronic mobility, the band gap and the acceptor-chromium ionization energy.

I - INTRODUCTION

Presently, the nature of majority defects responsible for the electronic conduction within pure rutile is still the subject of discussion in spite of numerous studies devoted to this topic and the varied experimental techniques used to determine it. Thus, the point defects proposed in the literature are either oxygen vacancies /1/ or titanium interstitials /2,3,4/ or also a mixture of these two defects /5,6/ whose ratios vary with experimental conditions of temperature and partial pressure of oxygen. By reason of these discrepancies, electronic conduction has again been studied with a view to stating the precise nature of point defects by means of complex impedance spectrometry. Indeed, such a method allows us to determine the electronic conductivity with a great accuracy /7/. Nevertheless, experiments have shown the presence of impurities may strongly affect the results of measurements.

Mixed conduction (both ionic and electronic) was shown off particularly within the undoped rutile near stoichiometry occurring at T = 1273 K under P₀₂ ≈ 1 atm. Therefore, electrical conduction has been studied not only in pure rutile but also in doped samples. Doping with trivalent chromium has been chosen because such a cation does not introduce crystallographical complication as shear planes at least for the range 0 up to about 5 moles % Cr₂O₃ /8/. Moreover, this cation Cr³⁺ having an ionic radius of 0,63 Å similar to Ti⁴⁺ (0,68 Å) may be substituted for titanium and yields a solid solution as the E.S.R., data bears out /9/.
II - EXPERIMENTAL PROCEDURE

Six cylindrical polycristalline samples ($\phi = 5$ mm, $l = 20$ mm) were prepared from a powder pressed under 2,000 bars for 1 hr in an isostatic press.

The first sample, in pure rutile, was obtained from hydrolysis of titanium chloride in ammoniacal medium /10/. The electronic microsonde analysis did not detect any impurities beyond the detection threshold (50 p.p.m.) both before and after experiments.

The other samples were achieved from a mixture of pure rutile and 99.999% chromium nitrate so that five solid solutions with respectively 1, 2, 3, 4 and 5% atoms of chromium were obtained after decomposition of the nitrate. Conductivity measurements were carried out by a a.c. method by complex impedance spectrometry. The impedance measurements were performed in the frequency range $10^{-10}$ Hz with a classical Sauvy bridge and with a Hewlett-Packard 4342 A Qmeter in the frequency range $10^{-10}$ Hz. Two platinum wires were introduced at the sample's extremities before pressing and serve to assure good electrical contacts. The results have been obtained in the thermodynamic equilibrium at $T = 1273$ K for various partial pressures of oxygen. These pressures were established and measured near to the samples by the Duquesnoy and Marion method /11/ in the range $10^{-12}$ to 1 atm.

III - EXPERIMENTAL RESULTS

![Electrical equivalent circuit](image)

Fig. 1 - Electrical equivalent circuit for Pt-(TiO$_2$-Cr$_2$O$_3$)-Pt chain at $T = 1273$ K in the frequency range $10^{-10}$ Hz.

![Isothermal conductivity plots](image)

Fig. 2 - Plots of isothermal electronic conductivity $\sigma_e$ against the partial pressure of oxygen at 1273 K for various ratios $\frac{Cr}{Cr + Ti}$ ($\bullet 0\%$, $\Delta 1\%$, $\square 2\%$, $\circ 3\%$, $\triangle 4\%$ and $\Box 5\%$).

The measured impedances $Z'(v) + jZ''(v)$ were plotted in the complex plane for various $P_{O_2}$. The analysis of obtained diagrams in relation with the frequency $v$ of the applied sinusoidal voltage shows that the conductive chain Pt-(Cr$_2$O$_3$-TiO$_2$)-Pt can be interpreted from the electrical circuit represented in Fig. 1. Such a cir-
cuit comprised of three parallel branches. The first branch \( C \) represents the capacitance of the measuring cell. The second branch represents the ohmic electronic resistance \( R = \lim_{u \to 0} Z'(u) \) of the sample. Finally, the third branch \( Z_j \) is an impedance which represents both the ohmic ionic resistance of the bulk as well as the impedance of polarization at the electrodes. If a symmetrical chain is assumed by construction, electrode phenomena kinetically involve a transfer resistance \( R_t \) and a Warburg's diffusion impedance \( Z_d^{1/12} \) which thus reveal the partial blocking of ions next to each oxide-platinum interface. Contrary to the two first branches, this last branch did not always show up. In the pure rutile, it appears only under air or oxygen and in such a case attests to the presence of residual impurities whose detection is possible only under stoichiometric conditions. In the doped rutile, the third branch appears only in the \( P_{O_2} \) domain above \( 10^{-15} \) atm whatever the studied doping. As a matter of fact, ionic conduction becomes negligible in the \( P_{O_2} \) domain below \( 10^{-10} \) atm and the electrical circuit in Fig. 1 is then simply reduced to a parallel dipole \( (R_e, C_e) \). However, in all experiments, the electronic resistance \( R_e \) is determined by extrapolation at zero frequency with a very good accuracy (about 1%). Consequently, taking into account the geometric factor, the same holds true for the electronic conductivity \( \sigma_e \). The isothermal variations of \( \log \sigma_e \) as a function of \( \log P_{O_2} \) are represented in Fig. 2 for different dopings studied at 1273 K. For the pure rutile, the variations are linear with a slope equal to -0.20. For the doped rutile, the minimum conductivity \( \sigma_{min} = 1.61 \times 10^{-4} \Omega^{-1}cm^{-1} \) is the same whatever the doping. The corresponding partial pressure of oxygen denoted \( P_{O_2,min} \) is revealed as being inversely proportional to the concentration of chromium since it obeys the experimental law: \( P_{O_2,min} = 10^{-3} [Cr_{Ti}^X]^{-1} \). Lastly, the slope of conductivity-curve tends to -0.25 on the weak sides of \( P_{O_2} \).

IV - DISCUSSION

Within the frame of the theory of point defects, the value -0.20 of the slope of conductivity curve for the pure rutile demonstrates the existence of majority defects as being titanium interstitials in maximum state of ionization. Using the Kröger and Vink notation /13/, the equilibrium of the sample with the ambient oxygen pressure can be expressed by the following reaction:

\[
Ti_{Ti}^X + 2O_{o}^X \rightarrow Ti_{Ti}^{4+} + O_2(g) + 4e^-
\]

with the associated equilibrium constant

\[
K_2 = [Ti_{Ti}^{4+}]^n [P_{O_2}]
\] (1)

The electroneutrality condition is given by:

\[
n = 4 [Ti_{Ti}^{4+}]
\] (2)

By assigning \( u \) as the mobility of electrons, the theoretical expression of the electronic conductivity \( \sigma_e \) can be deduced from equations (1) and (2):

\[
\sigma_e = q u n = q u (4 K_2^{-1/5} P_{O_2}^{-1/5})
\] (3)

This expression agrees with experimental data.

When chromium is incorporated into the rutile with a total concentration \( [Cr_{Ti}] \) the mass-balance relation is expressed by:

\[
[Cr_{Ti}] = [Cr_{Ti}^X]
\] (4)

or

\[
[Cr_{Ti}] = [Cr_{Ti}^X] + [Cr_{Ti}^{3+}]
\] (5)

according to whether the substitutional impurity cation possesses a fixed-valence one less than that of the host, or a mixed-valence (the dopant is then distributed between two valence states \( Cr^{3+} \) and \( Cr^{4+} \)).

In this later hypothesis, the transition \( Cr_{Ti}^{3+} + Cr_{Ti}^{4+} \) introduces a new equilibrium:

\[
Cr_{Ti}^{X} \rightarrow Cr_{Ti}^{3+} + h^+
\]

which may be described by the mass action relation
in which $K_i$ is the equilibrium constant

$$K_i = \frac{K_d}{K_a} = \left[\text{Cr}^{4+}_{Ti}\right]_p \left[\text{Cr}^{2+}_{Ti}\right]^{-1} = N_v \exp \left(\frac{-E}{kT}\right)$$

(6)

relative to the thermal excitation across the band gap:

$$\phi = E^v + h^+$$

$N_c$ and $N_v$ are the density of states in the conduction and valence bands:

$$N_{c,v} = \frac{2}{h^2} \left(\frac{2\pi m^* kT}{\hbar^2}\right)^{3/2}$$

(8)

and $E_a$ and $E_v$ are respectively the acceptor ionization energy and the band gap.

In the two $E_a$ hypothesis, the effect of impurities modifies the electroneutrality relation which taking into account the experimental transition n-type - p-type becomes:

$$n + [\text{Cr}^{4+}_{Ti}] = p + [\text{Ti}^{4+}_{i}]$$

(9)

In the n-type conductivity zone, the electronic conductivity $\sigma_e = \sigma_n + \sigma_u$ is reduced to $\sigma_n = q u n$ and from Eqs (3), (5), (6), (7) relation (9) is written as:

$$6 n + q u (K_d + [\text{Cr}^{4+}_{Ti}]_p) - 6 n - q u K_d = 0$$

(10)

This expression is valid for the case of fixed-valence chromium ($K_d = 0$) as well as for the case of mixed-valence chromium ($K_d \neq 0$). Considering two separate experimental values of the partial pressure of oxygen, the two parameters $K_d$ and $u$ may be deduced from Eq. (12). The computation yields the constants $K_d = 8.8 \times 10^{-16}$ cm$^{-3}$ and $u = 0.07$ cm$^{-1}$, not equal to zero.

Consequently, the model of mixed-valence chromium must be considered as the best. Thus, on the assumption that the electronic mobility equals the hole mobility, the co-ordinates of the minimum conductivity given by $\sigma_{min} = 2 q u K_d$ and $P_{02} = 4 K_d K_a K_v^{-3/2} \left[\text{Cr}^{2+}_{Ti}\right]^{-1}$ allows us to determine the other equilibrium constants $2 \sigma_{min} K_d = 5 \times 10^{-16}$ cm$^{-3}$ and $K_2 = 5 \times 10^{-5}$ cm$^{-1}$ atm.

V - CONCLUSION

Comparison of isothermal conductivity-curves at 1273 K between pure and chromium-doped rutile allowed us on the one hand to confirm the existence of majority titanium interstitials $\text{Ti}^{4+}_{i}$ in pure rutile and on the other hand to determine the four parameters $K_i$, $K_d$, $K_v$, and $u$. From these, the theoretical electronic conductivities may be computed as a function of $P_{02}$ for the various dopings. Good agreement between experimental and theoretical data emphasizes the validity of the mixed-valence chromium model suggested previously by Tani /14/. This interpretation is all the more probable since $\text{Cr}^{2+}_{Ti}$ has been previously suggested by Flörke /8/ to explain the solubility of chromium into rutile and also by Mirlin /15/ to interpret some results of E.S.R.

Taking the effective mass $m^*$ equal to seven times the mass of the free electron (average value met for semiconductors with wide band in particular the rutile /16/) and taking Eqs (6), (7) into account, yields $E_g = 1.22$ eV at 1273 K. It can be seen that this value is high as some authors /17/ have already suggested. This energy must be compared to the band gap $E_g = 2.41$ eV deduced from Eqs (7), (8) It may be seen that the acceptor level is practically layed in the middle of the band gap.

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