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SYNTHESIS AND PROPERTIES OF CONDUCTING MATERIALS IN THE TiO$_2$ - SnO$_2$ SYSTEM

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Abstract.- TiO$_2$ submicronic powder have been synthesised by controlled hydrolysis of titanium tetraisopropoxide. The influence of reagents concentration has been investigated. Additions of Niobium result in spherical particles. Mixed powders of TiO$_2$-SnO$_2$ have been produced by hydrolysis of SnCl$_4$-SbCl$_3$ solutions containing the Nb doped TiO$_2$ particles. The SnO$_2$-TiO$_2$ solid solutions are easily formed from 1100°C. However, the incorporation of the specific dopants is limited. The electrical conductivity is a non-linear function of the composition.

I - INTRODUCTION.

Tin and titanium dioxides have the same rutile structure and form complete solid solutions at 1430 °C/1-2/. On the other hand, both oxides are oxygen-deficient and n-type semiconductors. The electrical conductivity is enhanced by appropriate doping, e.g. antimony for SnO$_2$ and niobium for TiO$_2$. The complete ionisation of donor levels introduced by these dopants occurs at lower temperature in SnO$_2$ than in TiO$_2$ so that at room temperature, the electrical conductivity of Sb-doped SnO$_2$ ($10^3$ $\Omega^{-1}$ cm$^{-1}$ in the films) is several orders of magnitude greater than that of Nb-doped TiO$_2$.

The temperature coefficient of conductivity of Sb-doped SnO$_2$ from room temperature up to 1100°C, permits applications as heating elements and electrodes. However, prolonged thermal treatments at temperatures higher than 1100°C result in the breakdown of the electrical properties because of the volatilisation of the Sn and Sb oxides and the reduction of Sb$^{5+}$ into Sb$^{3+}$/3-4/. On the other hand, it is known that TiO$_2$ doped by 1-3 at.% Nb exhibits high and stable values of electrical conductivity ($1-5$ $\Omega^{-1}$ cm$^{-1}$) up to 1350°C/6/. The question of whether TiO$_2$ can partially replace SnO$_2$ for high-temperature electrical applications is of great interest especially in SnO$_2$-coated ceramics for which previous investigations have been carried out/4-5/.

An obvious approach to answer the above question is to sinter mixtures of doped SnO$_2$ and TiO$_2$ particles and investigate the relevant electrical properties as a function of phase composition at high temperature.

This communication describes:

i - The synthesis of submicronic Nb-doped TiO$_2$ particles by controlled alkoxide hydrolysis. This method enables us to sinter packed powder compacts with excellent relative densities ($>95\%$) at temperatures as low as 1100°C, as shown by H.Kent Bowen and al./7-9/.

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ii- The synthesis of doped TiO$_2$-SnO$_2$ powders mixtures by precipitation of SnCl$_4$-SbCl$_3$ solutions containing the TiO$_2$ particles.

iii- The study of sintering, phase formation and electrical conductivity of compacted powders between 1100°C and 1400°C.

II. EXPERIMENTAL.

The TiO$_2$ powders were prepared by the controlled hydrolysis of a diluted isopropyl-alcohol solution of titanium tetraisopropoxide (Janssen). Water was dissolved in separate portions of alcohol. The concentrations range between 0.3 to 1.3 M H$_2$O. Niobium was added as ethoxide (Ventron). The powders were centrifuged and dried at 80°C. Particle sizes, yield of precipitation and delay time for turbidity were determined as a function of the reagents concentrations. Phase transformation and sintering of these powders were studied by dilatometric, thermogravimetric and X-ray diffraction measurements.

The TiO$_2$ powders doped with 1 at.% Nb were dispersed in alcoholic solutions containing SnCl$_4$ and SbCl$_3$ (Sb/Sn = 0.1) /9/. Tin and antimony hydroxides were precipitated on the TiO$_2$ particles with ammonia. The powders were calcined at 500°C, then pressed into discs ($\phi = 13$ mm) under a load of 8000 Kg/cm$^2$ and sintered between 1100°C and 1400°C. The electrical measurements have been described elsewhere /10/.

III. RESULTS AND DISCUSSION.

The induction times necessary for the titanium hydroxide nucleation have been plotted as a function of initial water concentration for two concentration of Ti(OC$_3$H$_7$)$_4$, e.g. 0.1 and 0.15M/1 on a logarithmic diagram (Fig. 1a). The rate of nucleation is inversely proportional to the induction time so that the slopes of Fig.1, close to -3, indicate that the rate = $k$(H$_2$O)$^3$. Hence, the third step of the hydrolysis reaction, e.g.:

\[
\text{Ti(O}_3\text{C}_3\text{H}_7)_4 + 3 \text{H}_2\text{O} \rightarrow \text{Ti(O}_3\text{C}_3\text{H}_7)_3(\text{OH})_3 + 3 \text{C}_3\text{H}_7\text{OH}
\]

appears to be the limiting process of the particle formation. This result is in agreement with that of Barringer concerning the hydrolysis of titanium ethoxide /8/. Fig. 1b shows that the yield of precipitation becomes appreciable (75 % and more) only when $(\text{H}_2\text{O}/\text{Ti(O}_3\text{C}_3\text{H}_7)_4) > 3$. This result confirms the interpretation of Fig.1 a.

The conditions compromising a good mixing of reagents prior to the nucleation and a good yield of precipitation are achieved for 0.15M Ti(OC$_3$H$_7$)$_4$ and 0.5 to 0.6M H$_2$O/11/. The particles precipitated with 0.6 M H$_2$O are shown in Fig. 2 a. The mean grain size is 0.3 μm. These particles are not really equiaxed but are rather multinuclear as previously observed /7/.

![Fig. 1a](image1.png)  
![Fig. 1b](image2.png)

Fig. 1 a - logarithm of delay time before turbidity versus initial water concentration

b - yield of precipitation versus initial water concentration.
When Nb ethoxide is added to the solution so that Nb/Ti=0.01, the behavior is quite different: the induction times are modified (Fig. 1a); the particle shape becomes equiaxed and spherical (Fig. 2b). The niobium precursor which is probably less stable than Ti(OC₂H₅)₄ appears to enhance the nucleation and the growth of the particles so that small particle flocculation is impeded and the grains are mononuclear.

Dilatometric measurements (Fig. 3) performed on an amorphous TiO₂ compact show that most of the shrinkage occurs during the allotropic transformations: amorphous → anatase → rutile. The shrinkage involved in the last transformation (11%) is greater than that predicted by the crystallographic transition anatase-rutile (2.5%). A rearrangement of the particles occurs and induces a suitable packing for the sintering step. This step has a maximum speed around 1100°C so that appreciable densities (>90%) can be reached from this temperature.

The Sb-doped tin oxide precipitated on amorphous and rutile TiO₂ consists of fine crystallites as shown by the X-ray peak broadening observed up to 800°C. These powders are very reactive and form solid solutions at 1100°C. At 1400°C, the lattice parameters measured from the (220), (200), (101) and (211) X-ray diffraction peaks indicate that complete solid solutions exist for SnO₂ concentrations less than 35% and more than 65%. This is consistent with the equilibrium diagram reported by Park/2/ (Fig. 5). The relative densities of these solid-solutions (Fig. 6) decrease with increasing SnO₂ content. In fact, the densification of pure and Sb-doped SnO₂ is difficult to perform as previously reported /12/.

The green pellets of SnO₂-TiO₂ mixed powders exhibit electrical conductivity values ranging from 10⁻⁷Ω⁻¹ cm⁻¹ (100% SnO₂) to 3.5 10⁻²Ω⁻¹ cm⁻¹ (50% SnO₂) at room temperature, whereas the Nb-doped TiO₂ pellets are insulating (<10⁻⁷Ω⁻¹ cm⁻¹).
After firing at 1100°C and 1400°C, the Nb-doped TiO₂ samples become conducting \((\sigma=10^{-4} \Omega^{-1} \text{cm}^{-1})\). The Sb-doped SnO₂ remains conducting after these treatments. On the other hand, the doped SnO₂-TiO₂ mixtures are less conductive than the single doped oxides in the overall range of compositions. The addition of Sb-doped SnO₂ to Nb-doped TiO₂ in the one-phase region (up to 35% SnO₂) lowers the conductivity to a large minimum corresponding approximately to the two-phases region. It is likely that 

i/ the relevant lattice expansion impedes the charge transfer between the Ti and Nb cations

ii/ the solubility of Sb\(^{5+}\) in this phase is poor

On the other hand, the addition of TiO₂ to Sb-doped SnO₂ perturbs the band conduction of the last oxide to a significant extent so that the donor action of the dopants is less efficient.
IV. CONCLUSION.

Nb and Sb-doped SnO$_2$-TiO$_2$ solid solutions are easily formed (at $T > 1100^\circ$C) by the liquid mix technique described above. The specific donor effects of Nb$_{5+}$ and Sb$_{5+}$ decrease as TiO$_2$-SnO$_2$ solid solutions are formed. The electrical conductivity has a minimum in the two-phases region. The best conditions compromising the electrical properties and the chemical stability are to be found in the SnO$_2$ rich region of the binary diagram for TiO$_2$ content less than 20%. Such compositions can also be deposited by vapor pyrolysis and some preliminary experiments show that such films are more stable at 1200°C than the Sb-doped single SnO$_2$ films.

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