

Electrochromic properties of Nb₂O₅ and Nb₂O₅:X sol-gel coatings (X = Sn, Zr, Li, Ti, Mo)

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ABSTRACT

Two-layer coatings of Nb₂O₅ and niobia doped with tin (up to 15 at %), zirconium (up to 15 at %), lithium (up to 15 at %), titanium (up to 30 at %) and molybdenum (up to 30 at %) have been prepared by the sol-gel process and deposited by dip-coating on conductive ITO coated glass ($R_{\square} = 10 \Omega_{\square}$). They have been sintered in air between 450 °C and 600 °C. Their structure, morphology, electrochemical and optical properties (measured in a liquid electrolyte (1 M LiClO₄ in PC)) are reported. All systems exhibit electrochromic properties. Those are essentially determined by the structure and the morphology of the layers which can be changed in a controlled manner by the amount of doping and the sintering temperature. After Li⁺-insertion all amorphous coatings present a brown color, a blue one when the structure is hexagonal and a gray one when the structure is orthorhombic (pure, titanium or molybdenum doped niobia) or monoclinic (Li-doped niobia). Samples with two different structures color either blue or gray.

Keywords: Nb₂O₅, doped niobia, electrochromism, coating, sol-gel

1. INTRODUCTION

Since the observation by Reichman and Bard [1] of a coloring effect in Nb₂O₅ under H⁺ or Li⁺ insertion, several works have been published about the electrochromic behavior of this material [2-11]. The common feature observed with coatings made by DC magnetron sputtering or by sol-gel process using alkoxide, colloidal or polymeric sols is that amorphous Nb₂O₅ colors brown while crystalline Nb₂O₅ colors blue. Few studies have been published about the electrochromic behavior of doped niobia. Avellaneda et al. [12] prepared a Nb₂O₅-TiO₂ sample by sol-gel process and dip-coating. With a film sintered at 450 °C they observed a blue color after Li⁺-insertion. Macek et al. [10,13] obtained interesting results with Nb₂O₅:Li, also prepared by the sol-gel process. After lithium intercalation, a sample sintered at 500 °C exhibited a transmission of less than 10 % in the UV-Vis range. The color was gray.

The present paper presents a systematic study of the structure, morphology and electrochromic properties of 2 layers coatings of pure niobia and Nb₂O₅ doped with various concentrations of Sn, Zr, Li, Ti or Mo obtained by the sol-gel process and sintered at temperature ranging between 450 °C and 600 °C.

2. EXPERIMENTAL

All films were prepared using the sol-gel process. The niobium solution was obtained using a sonocatalytic process as described elsewhere [12]. A 0.4 M niobium solution was prepared by dissolving NbCl₅ (ChemPur) in ethanol and acetic acid. The doping at different concentration was realized by dissolving in ethanol SnCl₄ (Fluka) for tin, ammoniumzirconate (Fluka) for zirconium, LiCF₃SO₃ (Fluka) for lithium, titaniumisopropoxide (Fluka) for titanium or phosphormolybdenumacid (Fluka) for molybdenum. The solutions were mixed with the niobium solution and then subjected to an ultrasonic treatment for 2 min. All solutions were transparent. The coatings were deposited on In₂O₃:Sn (ITO) coated glass substrates (4x8 cm², Asahi, 10 Ω_{\square}) by dip-coating technique at a withdrawal rate of 2 mm/s. The films were dried at room temperature and submitted to a two step heat treatment at 100 °C and 450 °C during 30 min. The whole procedure was carried out two times and then the samples were sintered for 30 min at different temperatures ranging between 450 °C and 600 °C. The resulting films were homogeneous, transparent and had a thickness of 60 to 90 nm for one dip. The niobium content in each solution was kept the same, so that any change in the film thickness and measured property could be attributed to the content of doping ions.

Differential thermal analysis (DTA) and thermo gravimetric (TG) measurements were performed using a ST 501 equipment (Bähr) at a rate of 10 K/min. A mass spectroscopy analysis of the effluents was realized using a Thermolab 1165 (Fisons Instruments) coupled with the DTA/TG instrument. The structure was determined by X-ray diffraction measurements.

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They were performed at glancing incidence with a Siemens D 500 instrument with CuK _{α 1} radiation on 2-dip coatings.

The electrochemical and in situ optical measurements were realized using an EG&G 270 A potentiostat (Princeton Applied Research) and a three electrode cell. The two opposite sides of the cell were closed by the working electrode and a quartz window respectively. The counter electrode was a platinum foil and the reference electrode was a 0,01 M solution of Ag/AgClO₄ dissolved in the used electrolyte. The electrolyte was a 1 M solution of LiClO₄ dissolved in propylene carbonate (PC). The intercalation/desintercalation of the lithium ions was studied by voltammetry (scan rate: 50 mV/s) and chronoamperometry (Li⁺ insertion and desintercalation for 120 s between -2.2 V and +1.0 V vs. Ag/AgClO₄).

The optical spectra in the ultraviolet-visible-near infrared (UV-Vis-NIR) range were recorded in situ with a CARY 5E spectrophotometer (Varian). The transmission spectra were measured before (T_{bleached} , bleached state) and after (T_{colored} , colored state) insertion of Li⁺-cations. The change of optical density was calculated from these measurements according to $\Delta OD = -\log(T_{\text{bleached}}/T_{\text{colored}})$.

3. RESULTS AND DISCUSSION

3.1 PURE NIOBIUM(V)OXIDE

DTA/TG measurements have been conducted with a xerogel prepared from an undoped Nb₂O₅ precursor dried at 100 °C (fig. 1). In the DTA plot an exothermic peak is first observed at 250 °C. It is accompanied by a large mass loss involving essentially organic molecules (fraction of the solvent) (fig. 2 and 3). It is therefore attributed to the building up of an inorganic amorphous network. The second exothermic peak observed at 440 °C corresponds to the crystallization process (see also fig. 4). This peak is also accompanied by a smaller mass loss corresponding to the evolution of HCl and of fractions of organic molecules (fig. 2 and 3).

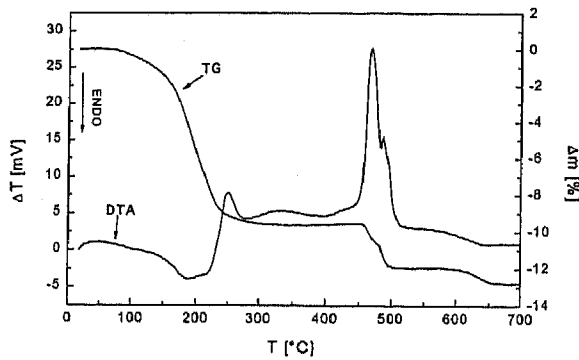


Figure 1: DTA/TG of a Nb₂O₅ xerogel (10 K/min).

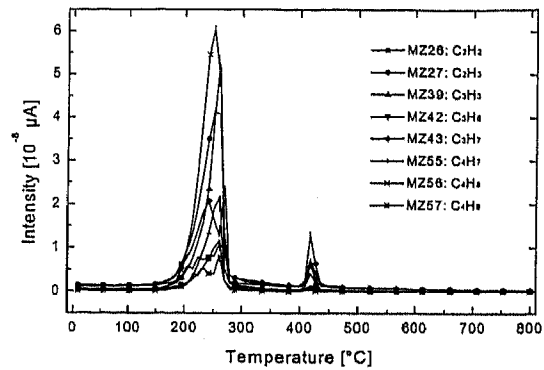


Figure 2: Mass spectroscopy of a Nb₂O₅ xerogel analyzed during the DTA/TG run of figure 1 (10 K/min).

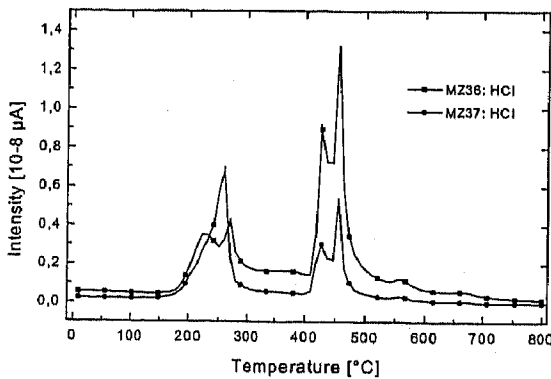


Figure 3: Mass spectroscopy of a Nb₂O₅ xerogel.

The structure and morphology of the coating depend on the sintering temperature (fig. 4). At temperatures $T < 460$ °C, they are amorphous. Nb₂O₅ layers sintered at 500 °C show a

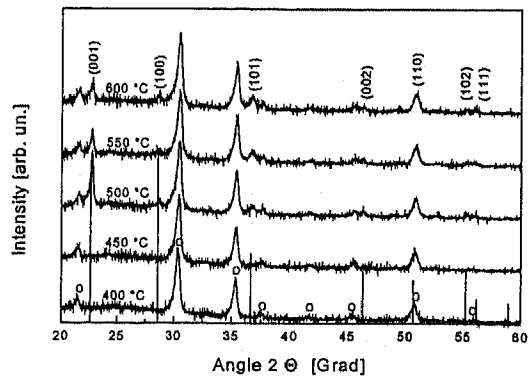


Figure 4: X-ray diffraction plot of undoped Nb₂O₅ sintered between 400 °C and 600 °C. O: ITO-peaks. Vertical lines JCPDS 28-317 data (hexagonal Nb₂O₅).

highly (001) oriented hexagonal structure with a crystallite size of ca. 70 nm. When sintered at 600 °C films have still the hexagonal structure but it is less oriented and the grain size is ca. 35 nm. The electrochromism of the layers and their relation with the structural change will be discussed later together with the doped systems. Experiments with different alcoholic solvents showed that the amount of lithium ions which can be inserted into the films and the corresponding change of the optical density both decrease with increasing length of the alkyl chain. In the following only results obtained using ethanol as solvent are reported.

3.2 NIOBIUM(V)OXIDE DOPED WITH LITHIUM

A DTA/TG plot of a xerogel prepared from a lithium doped niobia precursor shows the same peaks already observed for the undoped system (fig. 5). The formation of the inorganic amorphous network at ca. 250 °C and the crystallization process are also accompanied by a mass loss.

Different structures have been obtained depending on the amount of doping and the sintering temperature. All Nb_2O_5 :Li-samples sintered at 450 °C are essentially amorphous. Those sintered at 500 °C (fig. 6) are strongly crystalline and oriented (hexagonal Nb_2O_5 , JCPDS 28-317) in the undoped state and weakly crystalline and probably oriented (monoclinic LiNb_3O_8 , JCPDS 26-1176) in the doped state up to 10 % Li doping. The crystallite size (d) of the monoclinic structure is ca. 10 nm. The sample doped with 15 % Li appears amorphous again. The undoped Nb_2O_5 sintered at 600 °C (fig. 7) is still strongly crystalline with a hexagonal unit cell, but the crystallite size has decreased from 70 nm to 35 nm. The lithium doped samples are all built of two crystalline phases: a monoclinic LiNb_3O_8 one ($d \approx 10$ nm) and a hexagonal Nb_2O_5 one ($d \approx 40$ nm).

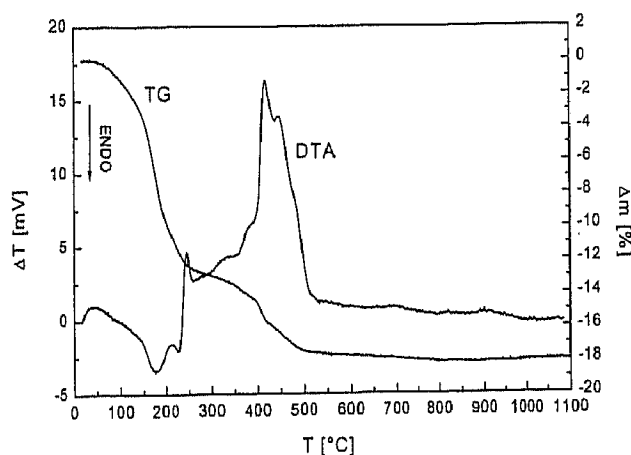


Figure 5: DTA/TG of a Nb_2O_5 :Li xerogel (10 K/min).

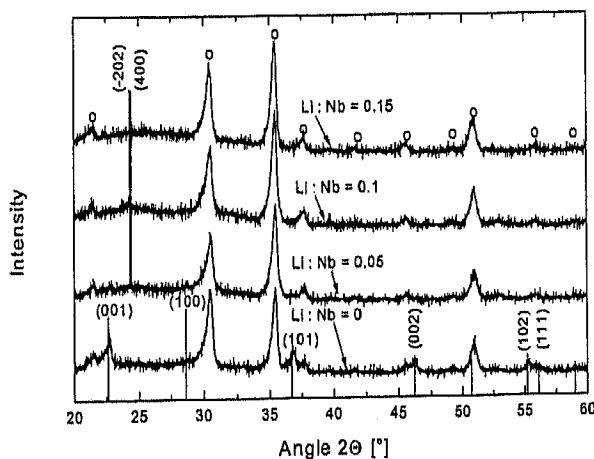


Figure 6: XRD-spectra of Nb_2O_5 and Nb_2O_5 :Li films sintered at 500 °C. O: ITO-peaks. Vertical lines at the bottom: JCPDS 28-317 data (hexagonal Nb_2O_5). Upper vertical lines: JCPDS 26-1176 data (monoclinic LiNb_3O_8). Both data fit the position of the experimental peaks.

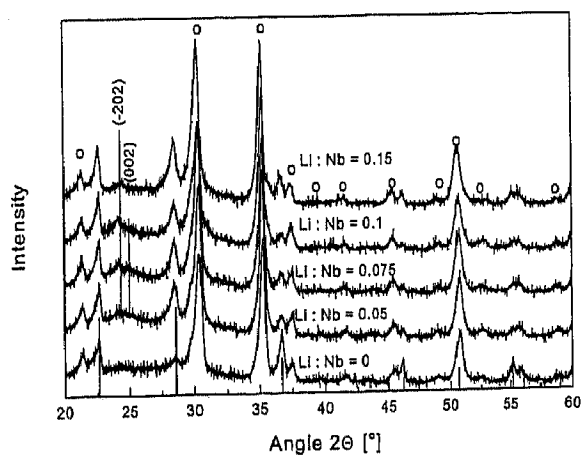


Figure 7: XRD-spectra of Nb_2O_5 and Nb_2O_5 :Li films sintered at 600 °C. O: ITO-peaks. Vertical lines at the bottom: JCPDS 28-317 data (hexagonal Nb_2O_5). Upper vertical lines: JCPDS 26-1176 data (monoclinic LiNb_3O_8). Both data fit the position of the experimental peaks.

The color observed by lithium intercalation depends on these structures (fig. 8 to 10). A brown color is found with all amorphous samples irrespective of the sintering temperature and the doping amount. Coatings exhibiting a well ordered hexagonal phase color blue and those which possess only the monoclinic structure color gray.

In the samples sintered at 450 °C the resulting absorption change (ΔOD) grows with the Li content up to 10 % Li and then decreases (fig. 8). The samples sintered at 500 °C show a different behavior (fig. 9). The overall spectral change of the optical density in the whole wavelength range remains nearly unaltered by the amount of Li doping when the structure is crystalline. But it decreases when the structure changes to amorphous. The maximum absorption in the visible range is observed with ca. 10 at % Lithium. The change of optical density for samples sintered at 600 °C is shown in fig. 10. The overall behavior is similar for all samples, but a decrease is observed for $\lambda > 750$ nm as the Li doping increases.

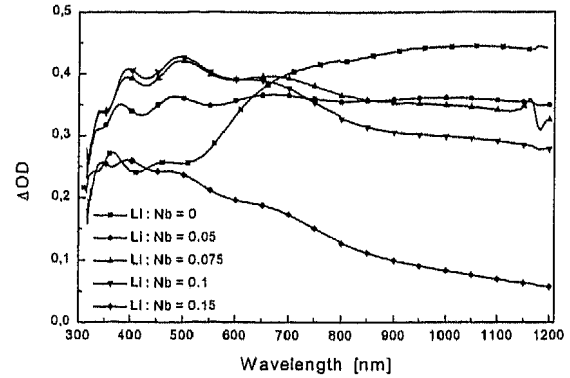
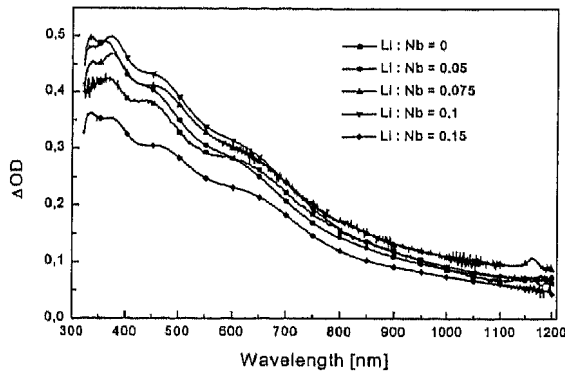


Figure 8: Spectral dependence of the change of the optical density of Nb_2O_5 and $Nb_2O_5:Li$ films sintered at 450 °C. Figure 9: Spectral dependence of the change of the optical density of Nb_2O_5 and $Nb_2O_5:Li$ films sintered at 500 °C.

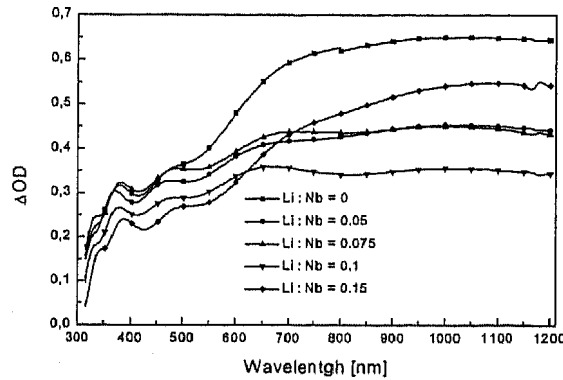


Figure 10: Spectral dependence of the change of the optical density of Nb_2O_5 and $Nb_2O_5:Li$ films sintered at 600 °C.

3.3 NIOBIUM(V)OXIDE DOPED WITH TITANIUM

The DTA/TG plots obtained with a xerogel prepared with a titanium doped Nb_2O_5 precursor show again the formation of the amorphous network at 250 °C and the crystallization process occurring at 490 °C (fig. 11). Both are accompanied by a mass loss.

Four different structures are observed as in the lithium doped niobia coatings (fig. 12 and 13). Again all samples sintered at 450 °C are amorphous. A strong (001) oriented hexagonal structure is found for the pure and up to 10 at % Ti doped samples sintered at 500 °C and 600 °C. At higher doping ($Ti:Nb=0.3$) the structure is again amorphous at 500 °C but a third phase appears at 600 °C for doping amounts of 20 and 30 at %. It consists of an orthorhombic structure of $Ti_2Nb_{10}O_{29}$ with a crystallite size of about 10 nm. At 20 at % Ti doping both the $Ti_2Nb_{10}O_{29}$ orthorhombic phase and Nb_2O_5 hexagonal phase coexist. Only the orthorhombic structure remains at 30 at % Ti doping.

The presence of the different phases affects the color of the coatings. The spectral change of all amorphous layers is identical and they exhibit a brown color when loaded with lithium ions. No significant change in the values of ΔOD could be reached by doping with titanium. The strongly ordered hexagonal structure leads to a spectral change identical to those seen with

$\text{Nb}_2\text{O}_5:\text{Li}$ sintered at $600\text{ }^\circ\text{C}$ and the resulting color is blue. The ΔOD values decrease with the amount of Ti doping. The resulting color after lithium ions intercalation was gray for all other samples, no matter if the orthorhombic XRD peaks appear alone (30 % Ti) or is accompanied by a peak linked to the hexagonal structure. The absorption in the visible range increases with the appearing of the orthorhombic structure and is the largest at 30 at % titanium doping.

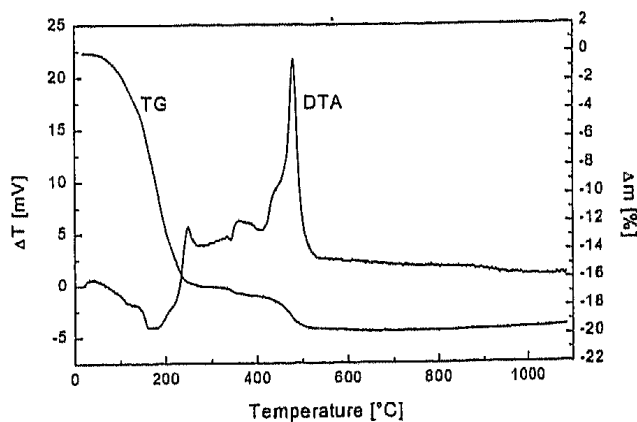


Figure 11: DTA/TG of a $\text{Nb}_2\text{O}_5:\text{Ti}$ xerogel (10 K/min).

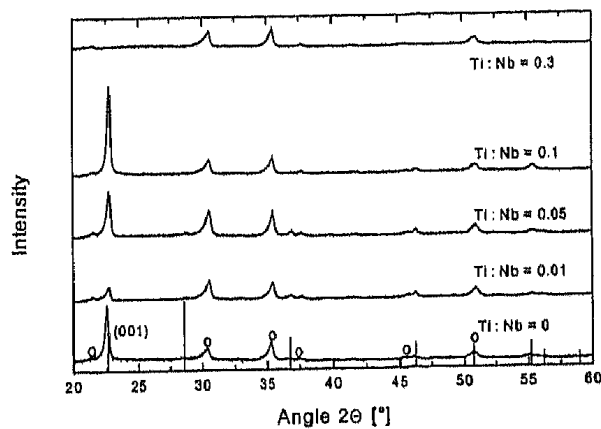


Figure 12: XRD spectra of Nb_2O_5 and $\text{Nb}_2\text{O}_5:\text{Ti}$ films sintered at $500\text{ }^\circ\text{C}$. O: ITO-peaks. Vertical lines: JCPDS 28-317 data (hexagonal Nb_2O_5).

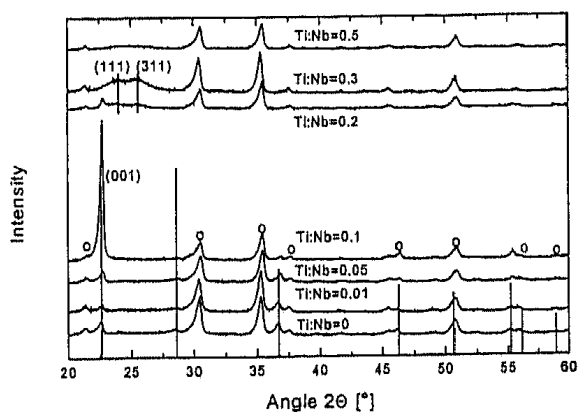


Figure 13: XRD spectra of Nb_2O_5 and $\text{Nb}_2\text{O}_5:\text{Ti}$ films sintered at $600\text{ }^\circ\text{C}$. O: ITO-peaks. Vertical lines at the bottom: JCPDS 28-317 data (hexagonal Nb_2O_5). Upper vertical lines: JCPDS 13-316 data (orthorhombic $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$).

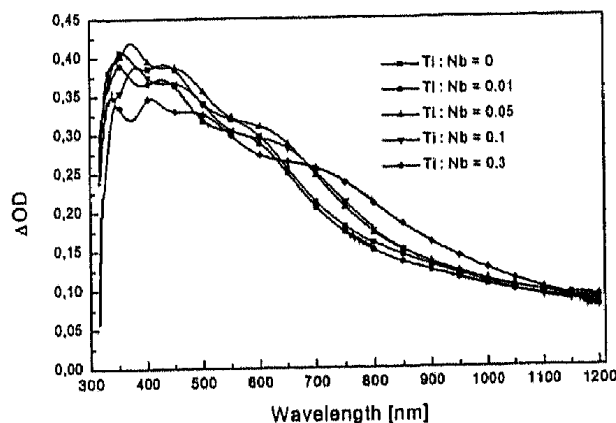


Figure 14: Spectral dependence of the change of the optical density of Nb_2O_5 and $\text{Nb}_2\text{O}_5:\text{Ti}$ films sintered at $450\text{ }^\circ\text{C}$.

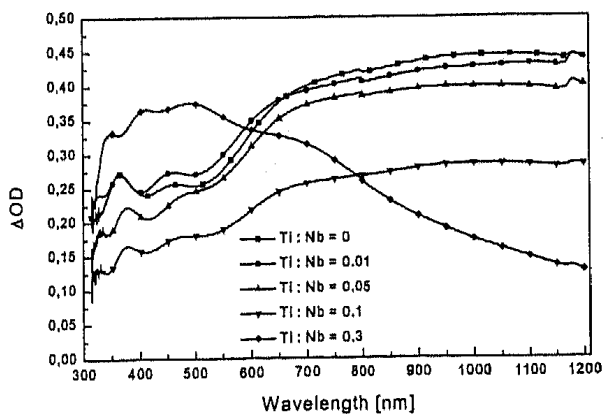


Figure 15: Spectral dependence of the change of the optical density of Nb_2O_5 and $\text{Nb}_2\text{O}_5:\text{Ti}$ films sintered at $500\text{ }^\circ\text{C}$.

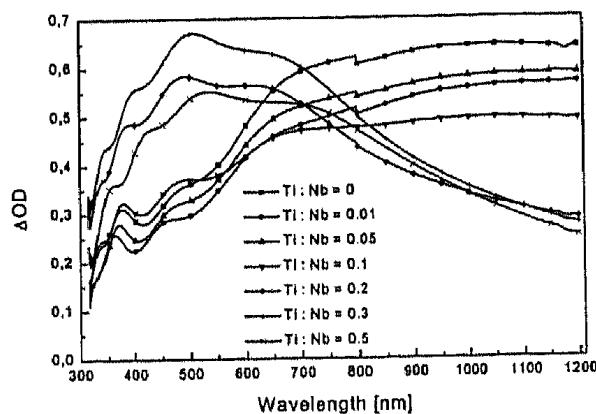


Figure 16: Spectral dependence of the change of the optical density of Nb_2O_5 and $\text{Nb}_2\text{O}_5:\text{Ti}$ films sintered at $600\text{ }^\circ\text{C}$.

3.4 NIOBIUM(V)OXIDE DOPED WITH MOLYBDENUM

The DTA/TG plot measured with a xerogel obtained from a 20 at % molybdenum doped Nb_2O_5 precursor reveals a well defined exothermic crystallization peak at 520 °C accompanied by a mass loss (fig. 17). It lays at a higher temperature compared to the measurements outlined before.

For the coatings it is observed four different structures according to the amount of doping and sintering temperature (fig. 18 to 20) and three different colors: brown, gray and blue after lithium ions intercalation depending on the structures (fig. 21 to 23). An amorphous structure is found for undoped Nb_2O_5 sintered at 450 °C, a pure (001) oriented hexagonal structure is observed for samples doped with 5 at % Mo sintered at 450 °C, with up to 10 at % Mo sintered at 500 °C and for the undoped niobia sintered at 500 and 600 °C. A pure weakly crystalline orthorhombic structure ($\text{Nb}_{12}\text{O}_{29}$) can be observed in films doped with 20 and 30 at % Mo sintered at 450 °C or 500 °C. The size of the orthorhombic crystallites is 15-20 nm. A mixed structure with hexagonal (Nb_2O_5) and orthorhombic ($\text{Nb}_{12}\text{O}_{29}$) crystallites is observed with a 10 at % Mo doping sintered at 450 °C and for all doped samples sintered at 600 °C.

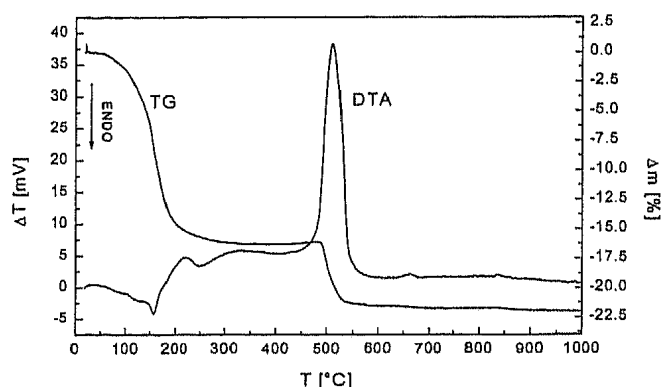


Figure 17: DTA/TG of a Nb_2O_5 :Mo xerogel (10 K/min).

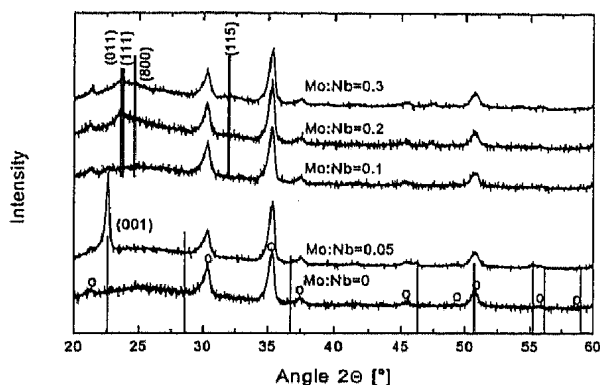


Figure 18: XRD spectra of Nb_2O_5 and Nb_2O_5 :Mo films sintered at 450 °C. O: ITO-peaks. Vertical lines at the bottom: JCPDS 28-317 data (hexagonal Nb_2O_5). Upper vertical lines: JCPDS 34-1169 data (orthorhombic $\text{Nb}_{12}\text{O}_{29}$).

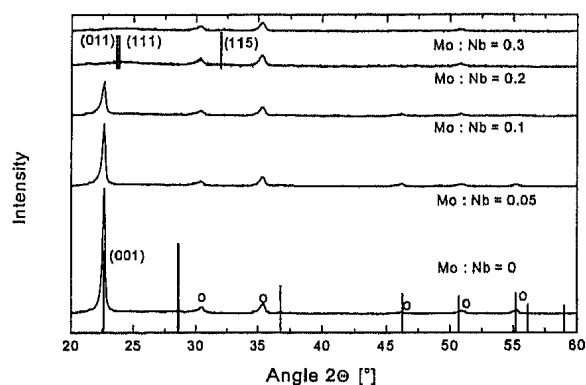


Figure 19: XRD spectra of Nb_2O_5 and Nb_2O_5 :Mo films sintered at 500 °C. O: ITO-peaks. Vertical lines at the bottom: JCPDS 28-317 data (hexagonal Nb_2O_5). Upper vertical lines: JCPDS 34-1169 data (orthorhombic $\text{Nb}_{12}\text{O}_{29}$).

The different structures again affect the spectral variation of the change of the optical density and the color of the coatings when Li^+ ions are inserted. The amorphous layers color brown, the strongly crystalline hexagonal ones color blue, those with the small orthorhombic crystallites color brown-gray. The respective spectral changes are similar to those presented earlier. The maximum value of the change of the optical density in the visible range occurred for coatings prepared with a molar ratio Mo:Nb=0.2 and sintered at 450 °C (fig. 21), for Mo:Nb=0.3 sintered at 500 °C (fig. 22) or at 600 °C (fig. 23). Hence, the orthorhombic structure with a morphology consisting of small crystallites shows the highest absorption variation.

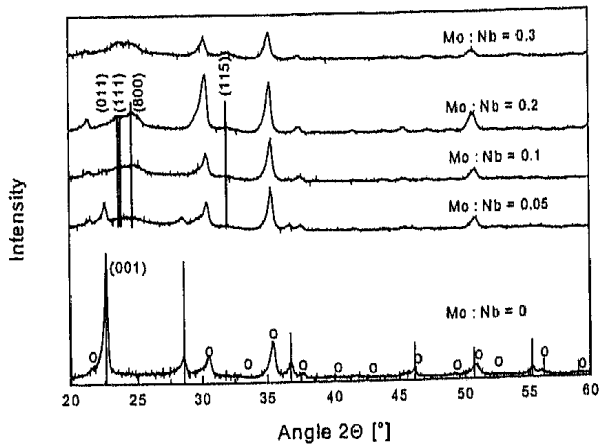


Figure 20: XRD-spectra of Nb_2O_5 - and $\text{Nb}_2\text{O}_5:\text{Mo}$ -films which were prepared at the sintering temperature 600°C . O: ITO-peaks. Vertical lines at the bottom: JCPDS 28-317 data (Nb_2O_5). Upper vertical lines: JCPDS 34-1169 data ($\text{Nb}_{12}\text{O}_{29}$).

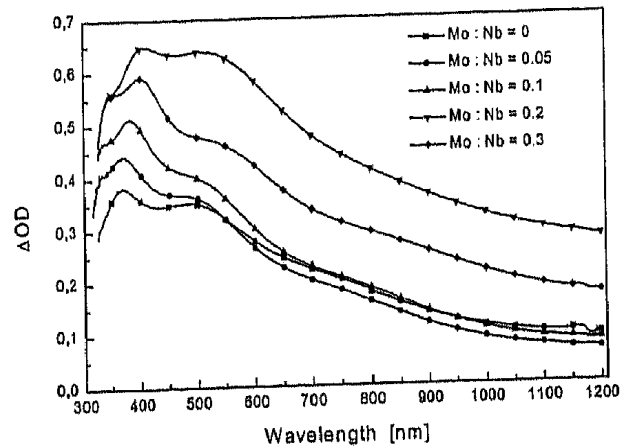


Figure 21: Spectral dependence of the change of the optical density of Nb_2O_5 and $\text{Nb}_2\text{O}_5:\text{Mo}$ films sintered at 450°C .

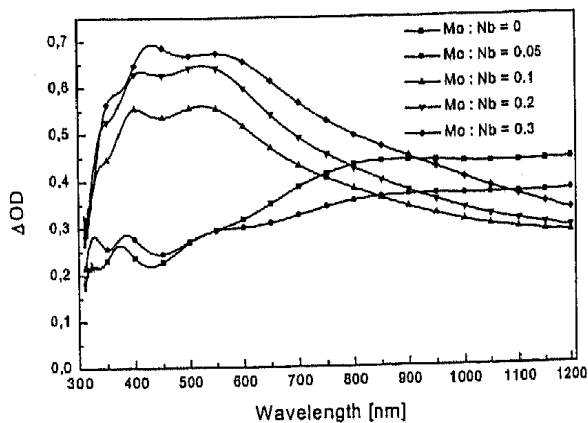


Figure 22: Spectral dependence of the change of the optical density of Nb_2O_5 and $\text{Nb}_2\text{O}_5:\text{Mo}$ films sintered at 500°C .

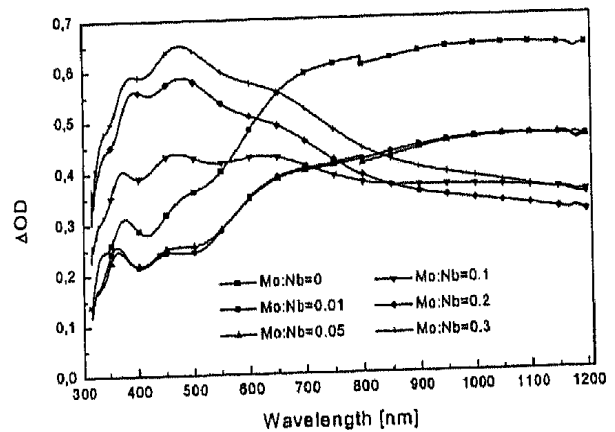


Figure 23: Spectral dependence of the change of the optical density of Nb_2O_5 and $\text{Nb}_2\text{O}_5:\text{Mo}$ films sintered at 600°C .

3.5 NIOBIUM(V)OXIDE DOPED WITH ZIRCONIUM OR TIN

The xrd plots of a pure and a 5 at % zirconium doped Nb_2O_5 coating (fig. 24) sintered at 600°C reveal no change in structure or crystallite size. For both materials the structure is hexagonal with a crystallite size of ca. 35 nm. After Li^+ -insertion a blue color is observed for coatings up to 10 % doping. The change of optical density decreases with increasing zirconium doping (fig. 25) and there is consequently no improvement by doping with zirconium. The same result was obtained with tin doped films sintered at 600°C (fig. 26).

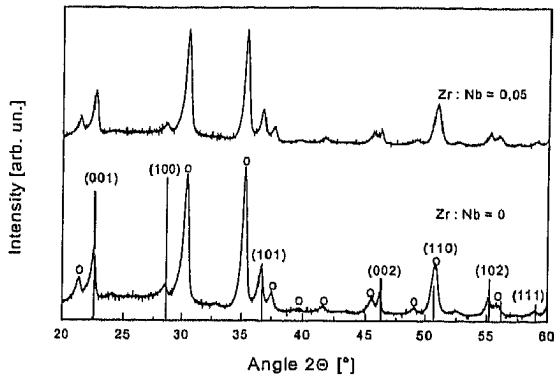


Figure 24: XRD-spectra of Nb_2O_5 - and Nb_2O_5 :Zr-films sintered at 600 °C. O: ITO-peaks. Vertical lines: JCPDS 28-317 data (hexagonal Nb_2O_5).

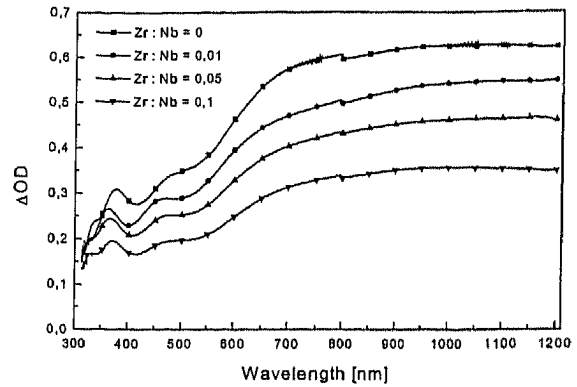


Figure 25: Spectral dependence of the change of the optical density of Nb_2O_5 and Nb_2O_5 :Zr films sintered at 600 °C.

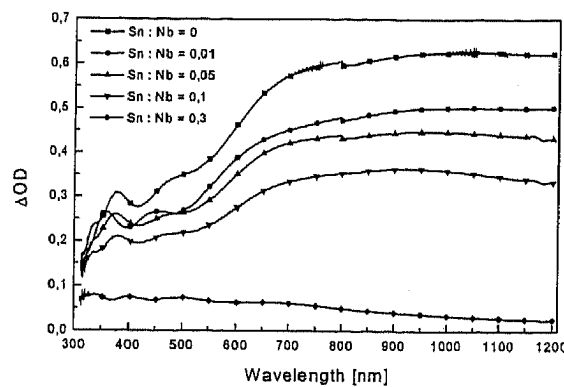


Figure 26: Spectral dependence of the change of the optical density of Nb_2O_5 and Nb_2O_5 :Sn films sintered at 500 °C.

4. INTERPRETATION

The doping of niobia has two interesting effects: a deeper coloring with the same amount of niobium atoms and the possibility to have a gray color in the intercalated state. Both effects seem to depend more on the crystallite size in the films or the degree of crystallinity than on the structure. Because of the small grain size obtained in the monoclinic and orthorhombic layers, the surface area and therefore the number of host places which can be reached by the intercalated ions in the lattice increases. The color which is observed after the loading seems to depend on the degree of crystallinity. With increasing crystallinity the absorption band shifts to higher wavelength. For the amorphous state it starts in the UV with a shoulder in the visible range. For samples with small crystallites up to 25 nm the absorption band lies essentially in the visible range. Finally, for well ordered samples with crystallite sizes over 30 nm the absorption band is in the NIR with a little shoulder in the visible range. Three typical spectra obtained with Nb_2O_5 :Ti coatings are shown in fig. 27 where the shift of the absorption band is clearly observed. In fig. 28 the wavelength of the maximum of ΔOD is plotted against the crystallite size for all data analyzed. We can distinguish three domains. First the amorphous samples (grain size $d \cong 0$) have their absorption maximum at wavelength smaller than 400 nm. They color brown. The coatings with a grain size up to 25 nm have a maximum absorption lying between 400 and 600 nm and they color gray. Finally the layers with grain sizes higher than 30 nm have an absorption maximum in the near infrared and have a blue color when lithium ions are inserted.

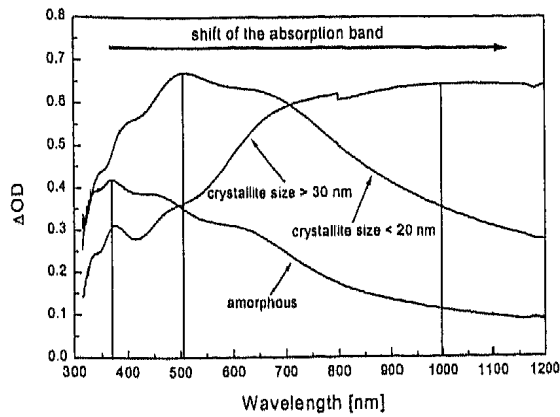


Figure 27: Typical spectra of ΔOD of a well ordered (crystallite size > 30 nm), a weakly ordered (crystallite size < 25 nm) and an amorphous $Nb_2O_5:Ti$ coating. The vertical lines mark the maxima.

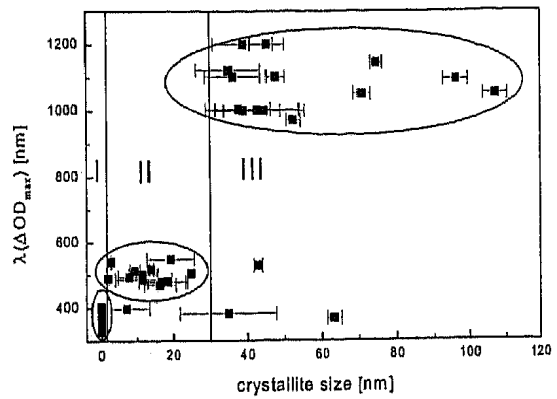


Figure 28: Wavelength of the ΔOD maxima vs. crystallite size of all undoped and doped Nb_2O_5 coatings discussed in this paper. For amorphous samples the crystallite size is „0“.

5. CYCLING STABILITY

The cycling stability of doped and undoped Nb_2O_5 films was tested up to 5,000 cycles. In fig. 29 ΔOD at 550 nm where the maximum of the sensibility of eye lies is plotted against the number of cycles. All tested coatings show a stable behavior. The change of optical density of the coatings increases during the first 100th cycles and then are practically stable. No dependence of the doping can be stated. From the point of view of stability all coatings seem to be capable to serve as electrochromic electrode in a thin film device [14].

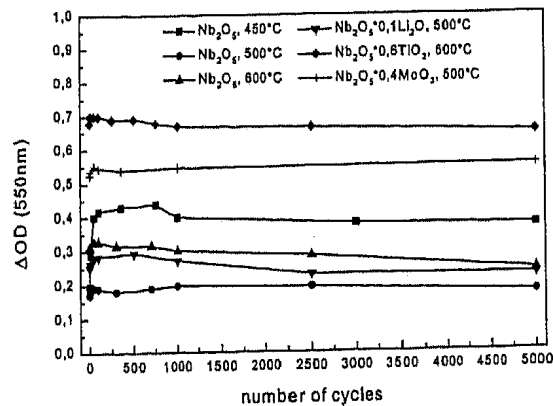


Figure 29: Cycling stability of doped and undoped Nb_2O_5 coatings.

6. CONCLUSION

The doping of Nb_2O_5 with ions like Li^+ , Ti^{4+} and Mo^{6+} in combination with the sintering temperature has a large influence on the structure, the morphology and the electrochemical behavior of the films. The amorphous samples (undoped or doped) color brown by lithium insertion. The Ti and Mo doped films with orthorhombic structure or Li doped films with monoclinic structure consist of small crystallites (5-20 nm) and color gray. The doped and undoped films with hexagonal structure consist of larger crystallites (35-100 nm) and color blue. The change of color in the colored state was discussed in term of the degree of crystallinity. The state of order or disorder (or an inbetween state) can be produced in niobia with different doping ions, by varying the amount of doping and the sintering temperature.

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