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ELECTRICALLY CONTROLLED COLORATION OF MATERIALS.(U)

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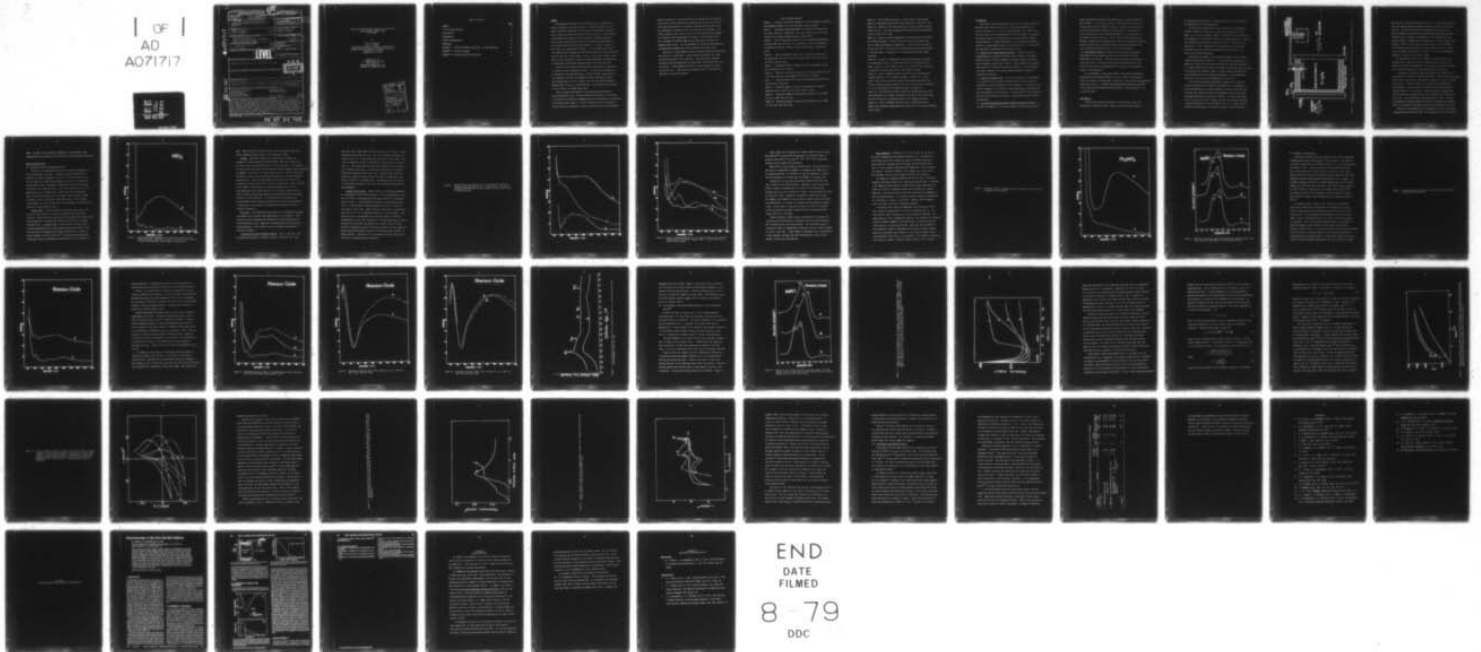
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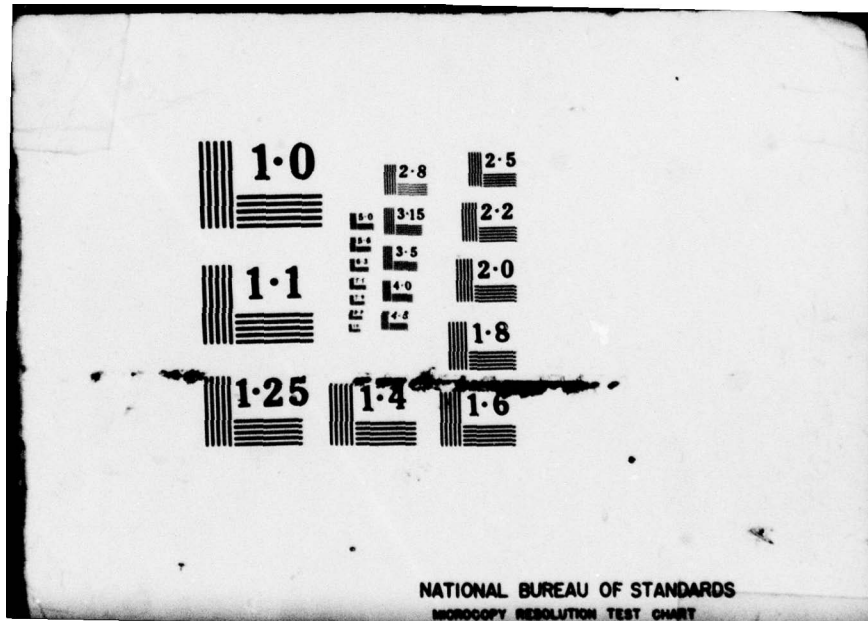
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
This report presents the results of a study of the phenomena of coloration of solid materials by application of electric potentials. Four specific aspects of this subject have been emphasized. First, new electrochromic materials were surveyed. Second, rhenium oxides were studied in detail to determine the origin of their thermochromic effect. Third, the rate-controlling mechanisms in liquid electrolyte cells were investigated. And fourth, various solid-state electrolyte materials were studied and one - termed PSSE - gave improved performance over those previously discussed in the literature.

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"Electrically Controlled Coloration of Materials"
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Summary

The phenomena of coloration of solid materials by application of electric potentials have been studied. Four specific aspects of this subject have been emphasized in our work at the University of Florida. First, new electrochromic materials have been surveyed. We established that rhenium oxide displays the electrochromic phenomena along with several metal tungstates and vanadium and tungsten phosphate glasses. Our current studies have shown that addition of a number of oxides to WO_3 results in a decreased EC response. All of the materials studied have shown absorption maxima near 100 nm and minima near 500 nm, therefore they have all been various shades of blue. However some mixtures showed shifts in the wavelength of absorption maxima suggesting the possibility of developing electrochromic materials with colors other than blue.

Second, we have studied rhenium oxides in more detail to determine the origin of their thermochromic effect. The data show that Re_2O_7 may be deposited by heating either ReO_2 or ReO_3 in vacuum. Re_2O_7 films are very hygroscopic and must be passivated towards adsorption of water. Upon heating Re_2O_7 in air or vacuum, a blue film is produced because of decomposition of Re_2O_7 to crystalline ReO_3 . This may also be the origin of the EC effect in rhenium oxide films.

Third, we have investigated the rate-controlling mechanisms in liquid electrolyte cells. The data indicate that the rate of coloration is initially controlled by a phenomenon that can be modelled as a resistance in the Butler-Volmer equation. After long times (≈ 1 sec.) the control switches from this mechanism to control by diffusion across the Helmholtz

layer in the EC cell. The initial rate of coloration may be controlled by the rate at which protons can be injected into the WO_3 film, and we have found that deposition of a porous conducting surface layer on the WO_3 considerably increases the rate of coloration and bleaching. This effect probably results from the fact that the conducting layer changes the electronic band bending near the surface of the WO_3 layer, and it also increases the field strength in the electrolyte to negate the Helmholtz layer effect. We have optimized the conducting layer material and deposition technique and a patent application has been filed.

And fourth, we have studied various solid-state electrolyte materials and found one - termed PSSE - to give improved performance over those previously discussed in the literature. With PSSE we have obtained coloration and bleaching speeds ten times faster than reported for other electrolytes. These speeds are similar to those obtained for liquid electrolyte cells. These data and processing steps for PSSE have been described in a patent disclosure.

List of Figure Captions

Figure 1. Schematic of an electrochromic cell used to measure coloration and bleaching response of an electrochromic film (e.g. WO_3).

Figure 2. Absorbance versus wavelength for a WO_3 film (A) before and (B) after coloration. Absorbance = $\log(I_0/I)$, where I_0 and I are the incident and transmitted beam intensity, respectively.

Figure 3. Optical absorption spectra for (V) an as-deposited 80% V_2O_5 -20% P_2O_5 glass film and (VC) its colored state. Curve (g) represents the glass with 2% V_2O_5 , 5% MoO_3 , 61% WO_3 , and 32% P_2O_5 in uncolored state.

Figure 4. Optical absorption spectra for (V) V_2O_5 - WO_3 films in the uncolored state and (h) for the heat treated films. (VC) and (hc) are for the EC colored films.

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Introduction

This final report describes the results of a three-year study into materials whose colored state can be altered by application of an electric potential (i.e. exhibit an electrochromic - EC - effect) and into the rate-controlling mechanisms of this color change. EC materials have great potential for display devices, and the ability to adapt a certain material to design requirements (i.e. environment and speed) is critical to technological success in the display area. As a result the study has been concentrated in four specific areas.

(1) Survey of new electrochromic materials. We have successfully demonstrated that rhenium and vanadium oxides, mixtures of WO_3 with rhenium, barium, rubidium, vanadium, and bismuth oxides, and several metal tungstates exhibit the EC effect. These materials were surveyed qualitatively for stability and spectral response. The data indicate that metal tungstates and vanadium-tungsten-phosphate glasses are promising EC materials.

(2) Studies of rhenium oxide. The EC and thermochromic (TC) behavior of powdered and vapor deposited rhenium oxides have been studied to determine the connection between EC and TC behavior. The stability and spectral response of the oxides have been measured and correlated with the oxide composition and structure. The data indicate that electrochromism and thermochromism are related to crystalline structure changes in this material.

(3) EC rate-controlling mechanisms in liquid electrolyte devices. To be used, for example, as a wristwatch display, EC materials must have

faster coloration and bleach (C/B) times than are currently reported in the literature. In the present work, we found that metal overlayers on the WO_3 could result in faster C/B times. A patent has been filed to protect the University's rights to this discovery.¹ In addition, we have investigated the rate-limiting mechanisms of coloration which are influenced by these overlayers. We have studied electrochemical cell kinetics, composite cell configurations, and current-voltage relationships. The data indicate that electrolyte double layers, WO_3 impedance, and surface Schottky barriers all play a role in EC coloration.

(4) Solid-state EC devices. Because of some possible technological advantages, we have surveyed various solid electrolytes for their application in EC devices. The intent was to decrease the C/B times of solid-state cells. One electrolyte worked exceptionally well in the devices, and a patent is being applied for to protect the University's rights to this discovery.²

In the remainder of this report we will first discuss experimental techniques and procedures pertinent to all four areas, then present in detail the results for these areas. Discussion of the results is incorporated within each section. In addition some experimental details are included in the results section where they are pertinent to the objectives of one of the four areas.

Experimental

With divergent specific objectives in the above four areas, the experimental procedures varied. However certain procedures common to

all areas are discussed here. Procedures specific to a given area may be discussed in the following section.

The starting materials used in this study were all commercially available powders from Cerac, Inc. (oxides and tungstates), or from McKay, Inc., or Alpha Inorganic (metals). Those used as thin films were vapor deposited from a heated crucible onto an oxide substrate. Generally this substrate was glass with a coating of SnO_2 (i.e. NESA glass, PPG Industries). Prior to deposition, the substrates were cleaned with detergent and water, rinsed with deionized water and alcohol, then placed in the deposition system.

Depositions were made in an oil diffusion pumped, liquid nitrogen trapped vacuum system at $\lesssim 5 \times 10^{-3}$ Pa. The system was not baked prior to deposition, however the oxide source material was generally outgassed at a low power setting with a shutter protecting the substrate from deposition. The substrates were normally heated to $\sim 100^\circ\text{C}$, however some deposition was performed without such substrate preheating. Typical deposition rates were ~ 2 nm/s and film thicknesses were ~ 0.2 - 0.6 μm .

The electrochromic and thermochromic response of the films was generally characterized by measuring the absorption in transmission. A Cary spectrophotometer was used to measure the response from 200 nm to ~ 2000 nm, and a Bausch and Lomb spectrophotometer was used for single wavelength measurements, typically at ~ 800 nm. For liquid electrolyte cells, the electrolyte was 1 N H_2SO_4 , and the coloration and bleaching response was measured in the cell shown in Fig. 1. A Luggin capillary connects the electrolyte to a saturated calomel reference electrode. A

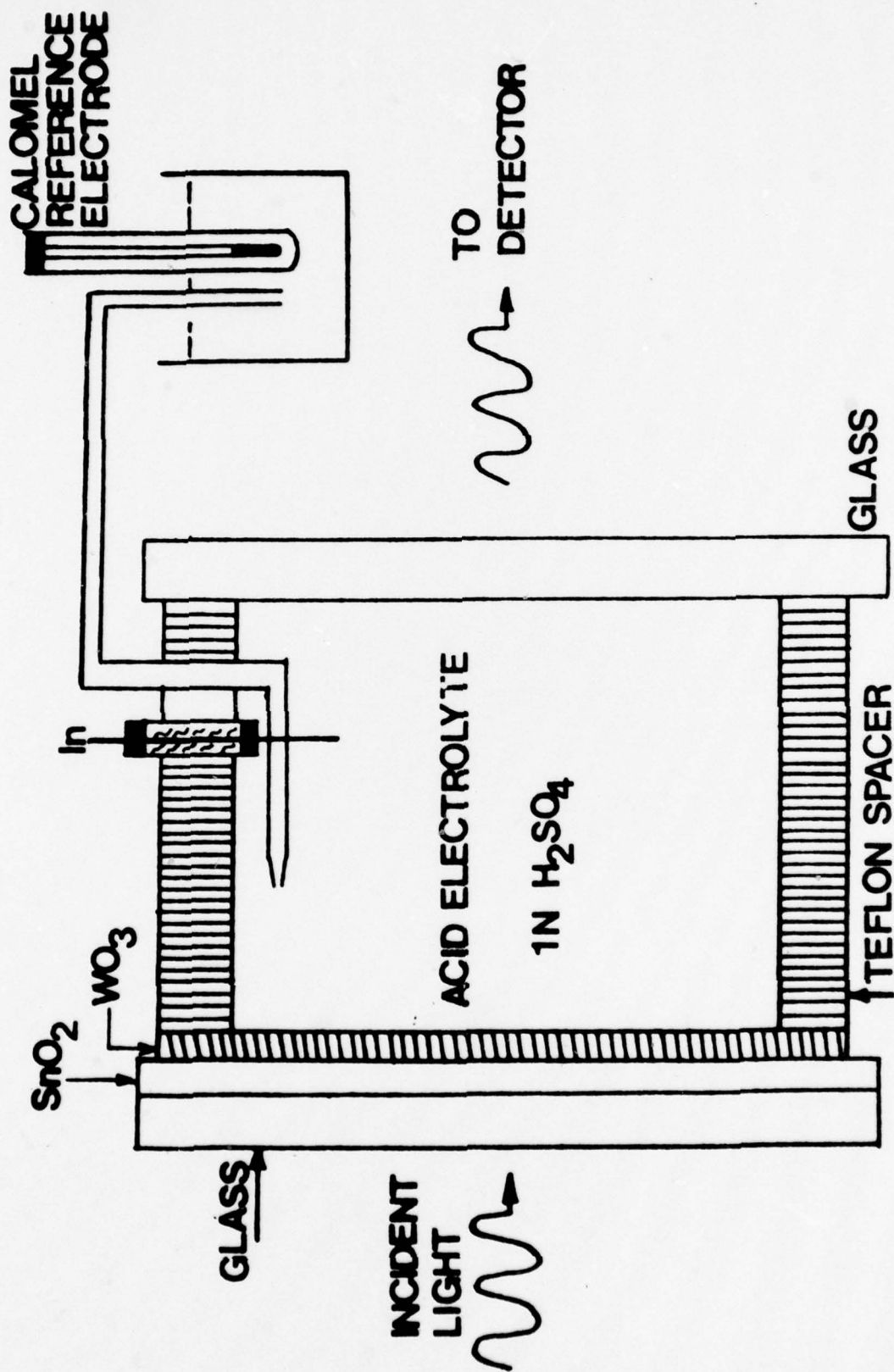


Figure 1. Schematic of an electrochromic cell used to measure coloration and bleaching response of an electrochromic film (e.g. WO₃).

metal counter electrode is mounted in the cell. In some cases reflection data were recorded simply by moving the detector around to the front of the film. Non-specular reflection was measured at an angle of $\sim 30^\circ$. Current flowing through the EC cell was measured and plotted along with absorption data, allowing a determination of the coloration per unit injected charge. Voltages were often supplied by constant voltage power supplies. However in the critical kinetic studies, the cells were EC colored using either galvanostatic or potentiostatic control, with the saturated calomel electrode as a reference. The counter electrode was normally Pt, although In was used at times.

To qualitatively check the EC response, some films were colored directly with 1 N H_2SO_4 into which an indium wire was inserted. As reported by Crandall and Faughman,³ this caused EC coloration presumably due to electrons injected by indium dissolution into the H_2SO_4 .

The powders and deposited films were characterized chemically and structurally by a number of different techniques. Rutherford backscattering (RBS)⁴ and particle induced x-ray emission (PIXE)⁴ were used to determine the quantity of elements present and to analyze the stoichiometry of oxides present. Auger electron spectroscopy (AES)⁴ was also used for elemental analysis on the surface. Elemental analysis throughout the film thickness was performed with AES in conjunction with sputtering by argon ions. X-ray photoelectron spectroscopy (XPS or ESCA - electron spectroscopy for chemical analysis)⁴ was used to determine the chemical state of the oxides at the surface and after sputtering into the films.

Structural characterization was accomplished by optical microscopy, scanning electron microscopy (SEM), and transmission electron microscopy

(TEM). For TEM, thin EC films were deposited on thin graphite films simultaneously with deposition on the previously described glass substrates.

Results and Discussion

(1) Survey of new electrochromic materials

Our work on the electrochromic effect has centered on mixtures of WO_3 with BaO , Re_2O_7 , and V_2O_5 . In addition we have studied the EC character of several tungstates (e.g. Ca, Sr, Ba, Ce, Rb, Na, Bi, Mg, Co, Mn, and Ni) and shown that the powder form of most of these can be electrically colored. Furthermore, tungstates of Ba and Sr have been deposited as thin films and shown to color electrically, but not to the same degree as in the powder form. Based upon Sakka's photochromic data,⁵ we have added Bi_2O_3 to both the powder and thin films of BaWO_4 and SrWO_4 to induce a different colored EC material. While dramatic color changes (e.g. blue to red) have not been produced, we have produced films with varying shades of blue.

Single oxides. The electrochromic oxides (WO_3 , MoO_3 , Re_2O_7 , and V_2O_5) have been studied as a basis for comparison with mixed oxide materials. WO_3 and MoO_3 were transparent after deposition and electrically colored deep blue, consistent with literature data (see, for example, references 6-8). As shown in Fig. 2, blue coloration in WO_3 results from strong absorption over a broad range centered near 1000 nm. V_2O_5 was light brown as deposited and turned blue-green after coloration, again consistent with the literature.^{8,9} Deposited rhenium oxide was translucent yellow, but switched upon application of a dc potential to

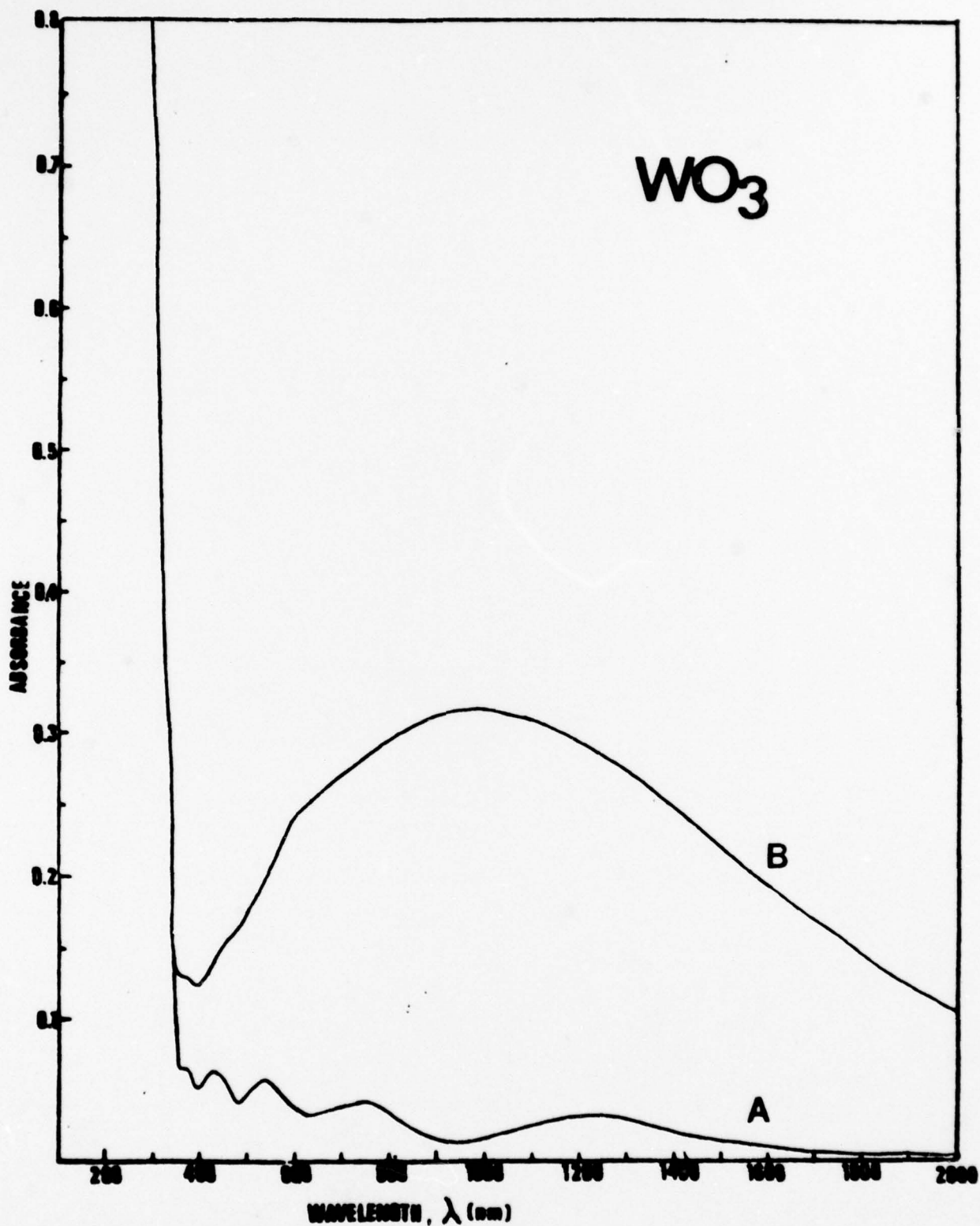


Figure 2. Absorbance versus wavelength for a WO_3 film (A) before and (B) after coloration. Absorbance = $\log(I_0/I)$, where I_0 and I are the incident and transmitted beam intensity, respectively.

blue. This is the first report of the EC effect in rhenium oxide and it will be discussed in more detail in the subsequent section.

BaO-WO₃. Mixed-oxide films of the system $x\text{WO}_3 + (1-x)\text{BaO}$ were prepared by co-evaporating WO_3 and BaO powders. Addition of BaO to WO_3 was found to have an inhibiting effect on color development. For example, 10 atomic % barium reduced the total amount of light absorbed electrochromically as compared to pure WO_3 . For barium concentrations of <10% the coloration inhibition is small, but at concentrations greater than 40% the inhibition approaches 90%. Films with approximately 10% barium were found to have a deep blue coloration upon removal from the vacuum system. This coloration can be removed by application of a bleaching potential of 1.5 volts. Sharp peaks were found in the diffuse x-ray diffraction patterns of the films at barium concentrations greater than approximately 45%, indicating the onset of crystallization. It is believed that the presence of a crystalline BaO phase is partly responsible for the coloration inhibition in these films. These results are described in reference 10 which is attached in Appendix 1.

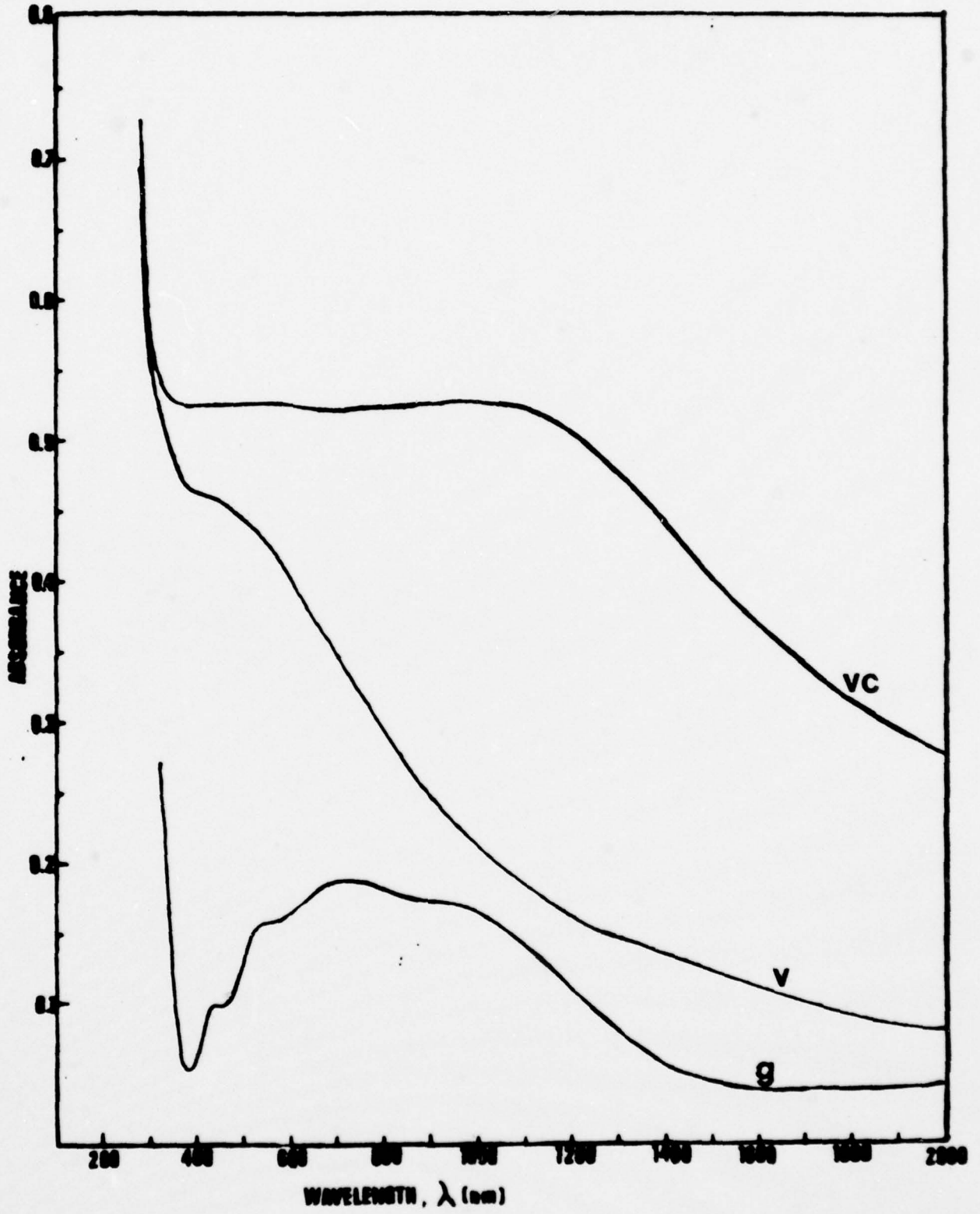
Re₂O₇-WO₃. Vapor-deposited films prepared by co-evaporation underwent a reversible blue coloration upon application of a dc potential. These films were quite deliquescent and therefore may be more appropriate for a solid-electrolyte cell. Additions of rhenium oxide to WO_3 resulted in strong inhibition of the EC effect even for rhenium concentrations of less than 10 atomic %.

V₂O₅-P₂O₅ and V₂O₅-P₂O₅-MoO₃-WO₃ glasses. Melts of 80% V_2O_5 : 20% P_2O_5 glasses were made in a platinum crucible at 1200°C in air. They

were cast onto a copper plate and heat treated at 250°C for 4 h. These glasses were dark brown in color. They were thermally evaporated at a pressure of 10^{-1} Pa to form transparent films with a brown color. They could be reversibly colored to blue-brown by application of a voltage (Fig. 3). Glass melts were also made with a composition of 2% V_2O_5 , 5% MoO_3 , 61% WO_3 , and 32% P_2O_5 . The bulk glass was blue, and evaporated films were transparent with a blue color. Although they could be EC colored to a deeper blue and could be bleached to a light blue, they would not bleach to a colorless film. The absorption spectra (Fig. 3) of this glass shows peaks at 400, 500, 700, and 900 nm with the 700 nm peak dominating.

$V_2O_5-WO_3$ and $V_2O_5-MoO_3$. Films of $xWO_3 + (1-x)V_2O_5$ were deposited by co-evaporation from different sources. These V_2O_5 additions to WO_3 have the effect of decreasing the band edge as shown in the absorption spectra in Fig. 4. Electrochromic coloration of these mixtures gives rise to a broad absorption peak extending from 0.65-1.2 μm (Fig. 4), resulting in a blue color. Apart from the characteristic electrochromic peak at 0.9 to 1.0 μm , an additional peak at 0.7 μm was observed. This peak was found to increase when the films were heated to $\sim 250^\circ C$ for approximately one hour after deposition. The band edge shifted to lower energies with increasing V_2O_5 additions in a manner similar to that reported by Bogomolova *et al.*¹¹ for $WO_3-P_2O_5$ glasses with V_2O_5 additions. However upon electrochromic coloration the band edge seems to shift to higher energies. Absorption in the transmission window between 250 and 550 nm also increased with V_2O_5 additions.

Figure 3. Optical absorption spectra for (V) an as-deposited 80% V_2O_5 -20% P_2O_5 glass film and (VC) its colored state. Curve (g) represents the glass with 2% V_2O_5 , 5% MoO_3 , 61% WO_3 , and 32% P_2O_5 in uncolored state.



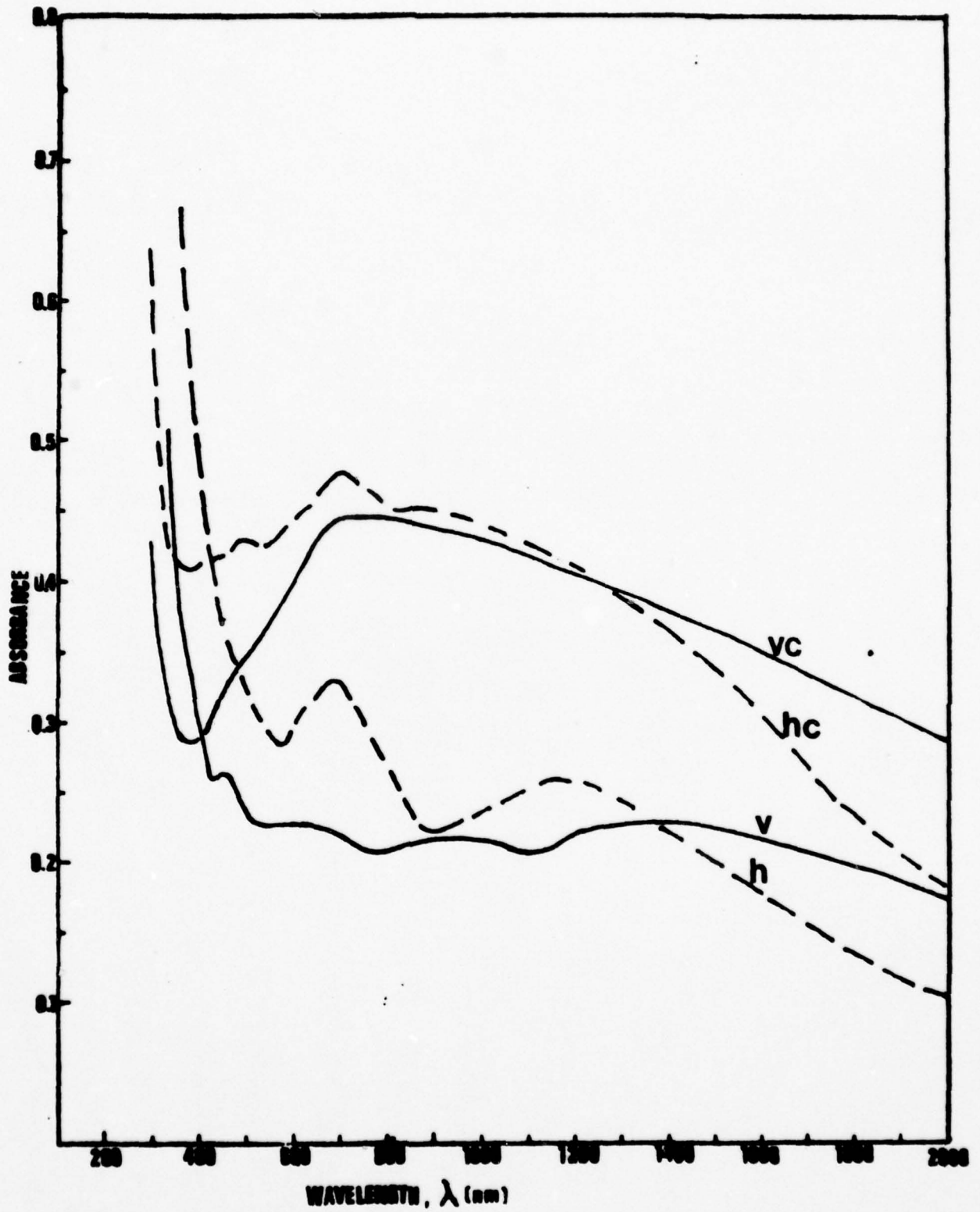


Figure 4. Optical absorption spectra for (v) $V_2O_5-WO_3$ films in the uncolored state and (h) for the heat treated films. (vc) and (hc) are for the EC colored films.

These results can be explained in a manner similar to that for WO_3 - MoO_3 mixtures¹² by saying that the absorption in the mixed oxides is caused by excitations of the type $W^{5+} + V^{5+} + W^{6+} V^{4+}$ and excitations increase with the degree of EC coloration.

Mixed films of V_2O_3 and WO_3 were also studied. The deposited films were grey but transparent as compared to transparent and light yellow for V_2O_5 - WO_3 mixtures. EC coloration of V_2O_3 - WO_3 resulted in a peak at ~ 900 nm and changes in the band edge were similar to V_2O_5 - WO_3 films.

Although all the V_2O_3 and V_2O_5 mixtures produced a blue EC color, their coloration rates were different. Additions of V_2O_5 and V_2O_3 were found to reduce the dissolution of the films into the electrolyte, although pure V_2O_5 was not stable in 1 N H_2SO_4 . The coloration efficiency and rates were found to depend on the amounts of added V_2O_5 or V_2O_3 . For example, small amounts of V_2O_3 caused the films to color less deeply upon application of a voltage, but response time was faster as compared to WO_3 . As the amount of V_2O_3 was increased, the depth of coloration could be increased with larger voltages and the films exhibited much longer open circuit lifetimes.

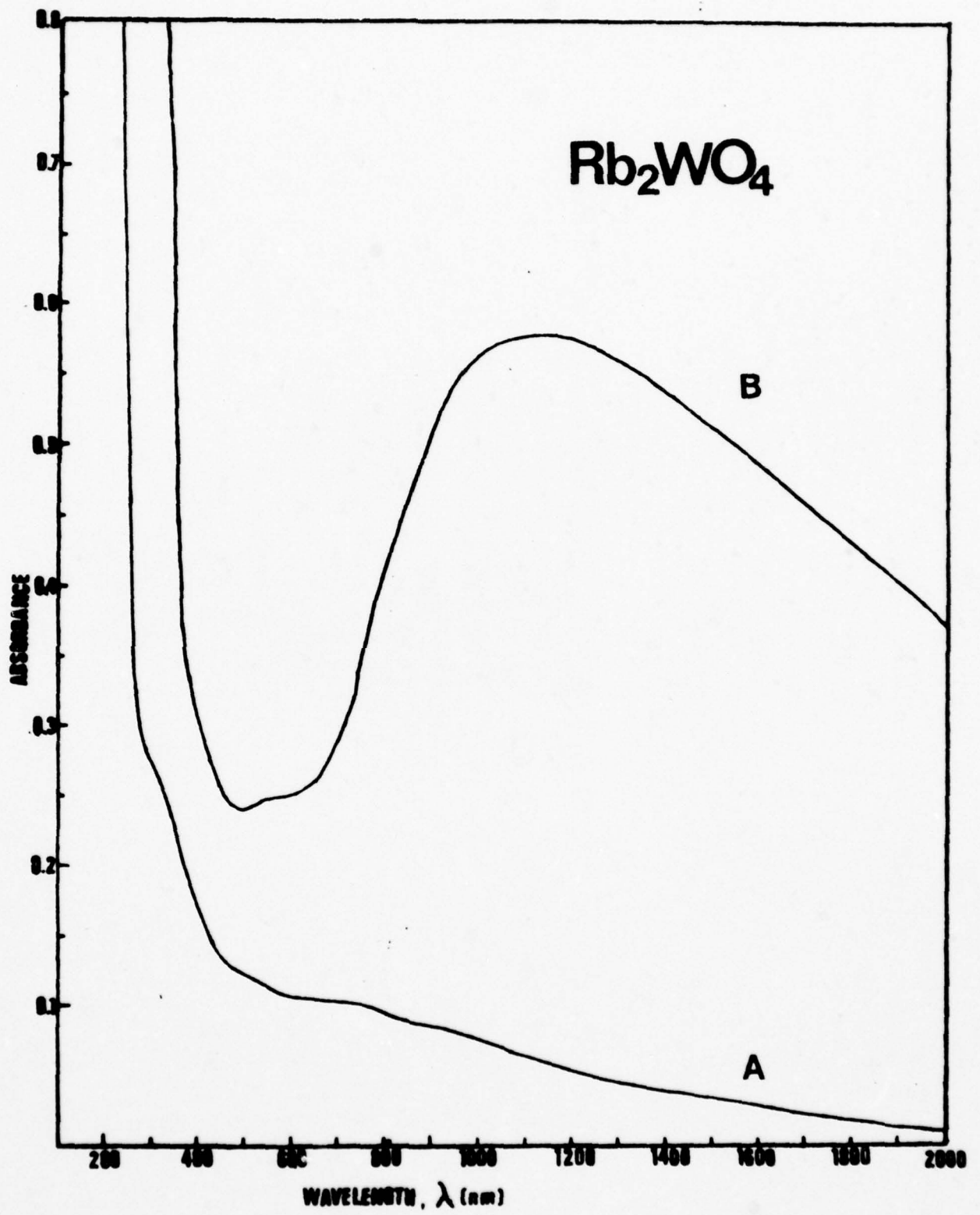
These preliminary studies indicate that mixtures of V_2O_5 - WO_3 and V_2O_3 - WO_3 have good potential for forming EC films with high efficiency, fast coloration speed, and long lifetimes. The possibility exists of varying the energy of maximum photon absorption, and as a result changing the color of the film. A small number of experiments with co-evaporation of V_2O_5 and MoO_3 indicates that electrochromism also occurs in this system. The EC color was deep blue.

Metal tungstates. Powders of Ca, Sr, Ba, Ce, Rb, Na, Bi, Mg, Co, Mn, and Ni tungstates were purchased from Cerac, Inc. The ability to electrically color these powders was tested by settling them onto a glass substrate, covering with dilute H_2SO_4 , and touching with an In wire.³ In all instances except Mn and Ni tungstates, a blue coloration was induced. Although no dramatic color changes (e.g. red vs. blue) were observed, the blue colors ranged from light blue to black.

The commercial tungstate powders of Na, Rb, Ba, and Sr were vapor deposited onto glass plates with a conducting tin oxide layer. Coloration in the $BaWO_4$ and $SrWO_4$ could be achieved with an H_2SO_4 electrolyte and either an In wire or a potential between the tin oxide and a counter electrode. The color was blue and the color depth was not equivalent to that of settled powders. The coloration could be bleached by application of a potential or of H_2O_2 to the surface. However, very few samples would color again after such a bleaching treatment.

The Rb_2WO_4 films turned blue immediately upon application of the acid, without the application of an electric potential (Fig. 5). The film could be erased with H_2O_2 but not with an applied potential. The Na_2WO_4 was blue in the as-deposited condition. The intensity of coloration could be increased somewhat by the application of a potential but the films could not be erased electrically. Based upon data by Sakka,⁵ we have conducted a number of experiments where Bi_2O_3 was added to $BaWO_4$. However our procedures only resulted in a blue electrochromic state in these materials (rather than a red coloration). The methods of production were varied to attempt to reproduce Sakka's results, but to no avail.

Figure 5. Absorbance spectra of RB_2WO_4 film (A) as-deposited and (B) after coloration with 1 N H_2SO_4 .



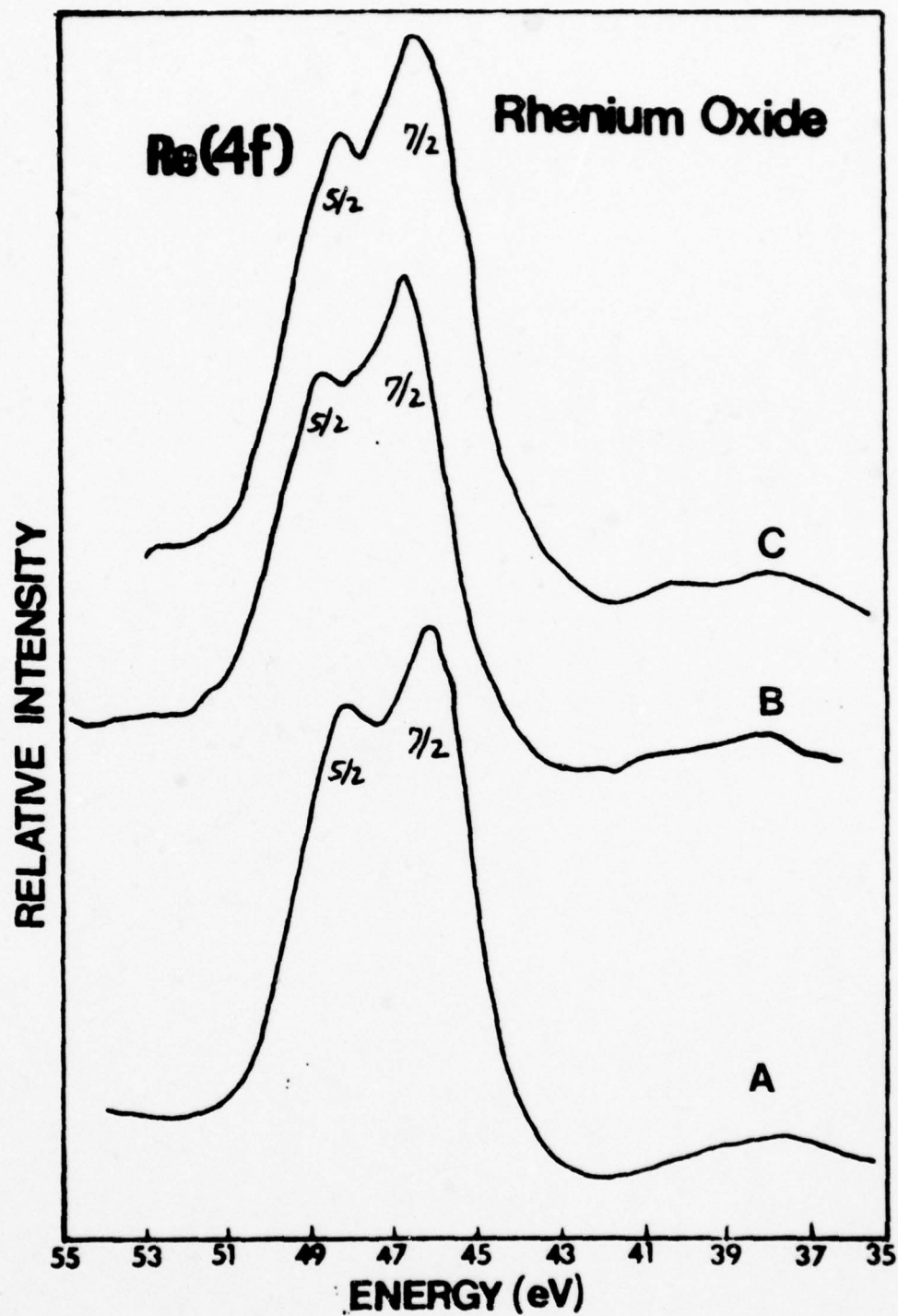


Figure 6. ESCA Re 4f core level spectra from (A) Re_2O_7 powder and from films vapor deposited from powders of (B) ReO_3 and (C) ReO_2 .

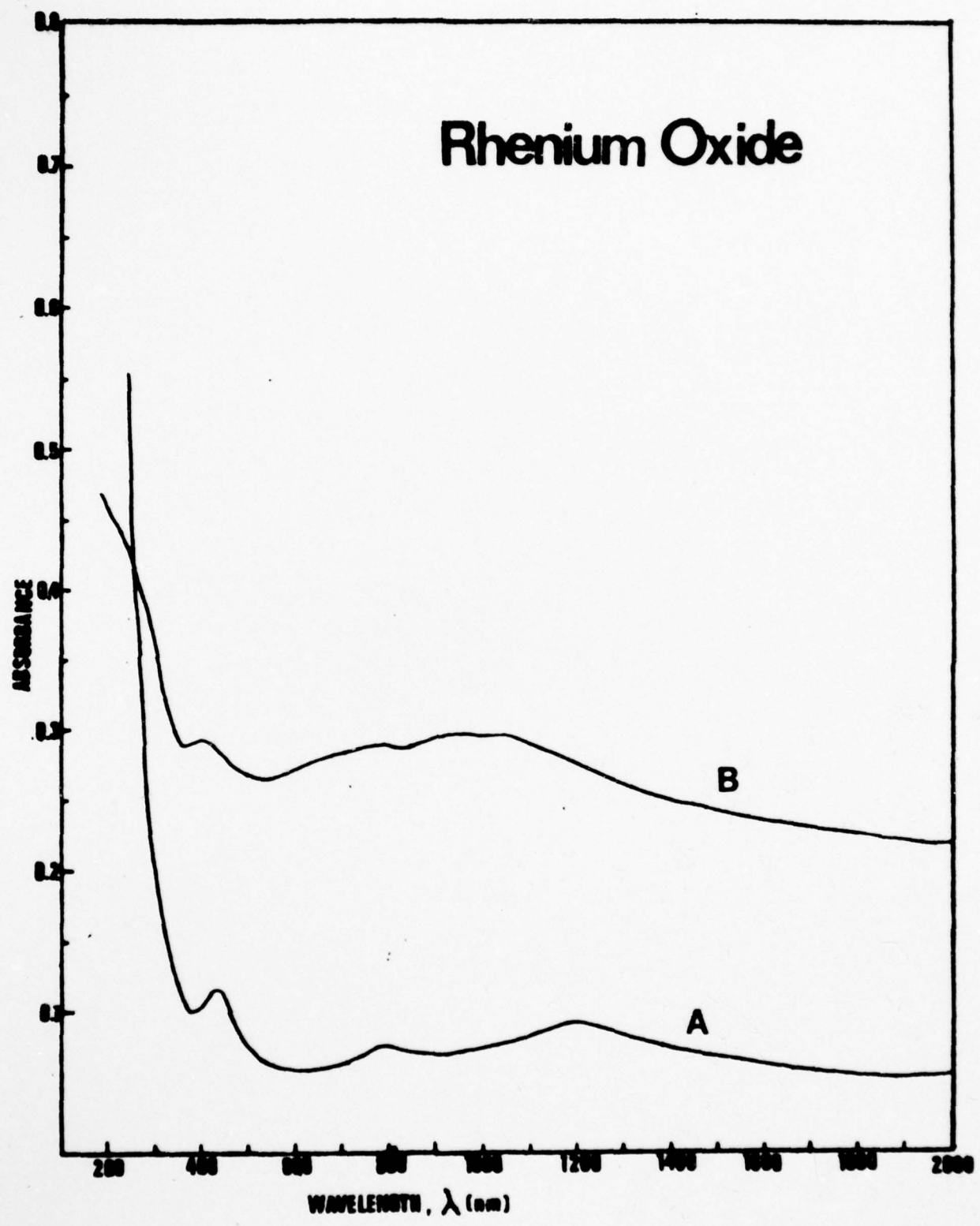
(2) Studies of rhenium oxide

Thin films of rhenium oxide were thermally evaporated and deposited on NESA glass and quartz from powders of ReO_2 and ReO_3 . The films had the physical characteristics reported for Re_2O_7 , i.e. they were hygroscopic and yellow in color. ESCA data indicate that films made from either ReO_2 or ReO_3 powder had the same electronic structure. Data in Fig. 6 show that the Re 4f photoelectron peaks from Re_2O_7 powder and from films deposited from ReO_2 and ReO_3 powders respectively are very similar. The Re peaks in Re_2O_7 are shifted to a higher binding energy ($4f^{7/2}$ binding energy of 46.2 eV) than those reported for ReO_3 ($4f^{7/2}$ binding energy of 43.2 eV),¹³ which is consistent with the higher valence state (Re^{7+}). The formation of Re_2O_7 as a decomposition product obtained by heating ReO_2 or ReO_3 in vacuum is also consistent with the findings reported by Druce.¹⁴

As reported earlier, films of Re_2O_7 exhibited a reversible EC effect when touched with an indium wire in the presence of 1 N H_2SO_4 , or when a small potential was applied across the film using the acid electrolyte.¹⁵ The film changed from transparent yellow to deep blue. Figure 7 shows the absorption spectra for a Re_2O_7 film before and after EC coloration. The blue coloration develops because of an absorption band with maxima at 700 nm (red) and 1100 nm (near infrared) and a minimum at 500 nm (blue). It is noted that only a portion of the irradiated area was colored, so that the spectrum of the colored film possesses some features of the original Re_2O_7 . Colored areas of Re_2O_7 sufficiently large for optical absorption measurements are quite difficult to obtain

Figure 7. Absorbance spectra for Re_2O_7 (A) as-deposited and (B) after electrochromic coloration.

Rhenium Oxide



electrochromically. The hygroscopic nature of the films results in a break-up and separation from the substrate in the area beneath the acid.

Because of its hygroscopicity, techniques to passivate the Re_2O_7 toward H_2O adsorption were studied. SiO layers ~ 400 nm thick effectively passivated the Re_2O_7 film toward absorption of H_2O from the atmosphere, but they were not sufficient to prevent the acid electrolyte from soaking through to the Re_2O_7 during coloration. The Re_2O_7 films could be EC colored with these SiO films in place.

Besides exhibiting an EC effect, Re_2O_7 also was found to exhibit a thermochromic (TC) effect. Heating the as-deposited films to 100°C to 150°C for times as short as 30 sec. resulted in coloration. Figures 8-10 show progressive changes in the optical absorption spectra as the time of heating at 150°C was increased. The heated films appeared blue or greenish-blue in transmission and red in reflection. After 3 min. of heating the absorption spectrum showed a broad band with a maximum at ~ 400 nm and an absorption minimum at 500 nm (blue). The colored state is retained upon cooling to room temperature but can be removed by bleaching with H_2O_2 . Similar effects were found during heating of Re_2O_7 powders.

The composition and structure of the Re_2O_7 films were studied to identify the origin of the TC effect. X-ray (Fig. 11) and electron diffraction data indicated that the as-deposited films were amorphous. Upon heating in air or vacuum, both x-ray (Fig. 11) and electron diffraction data indicated that crystallites of ReO_3 were formed. ESCA results were

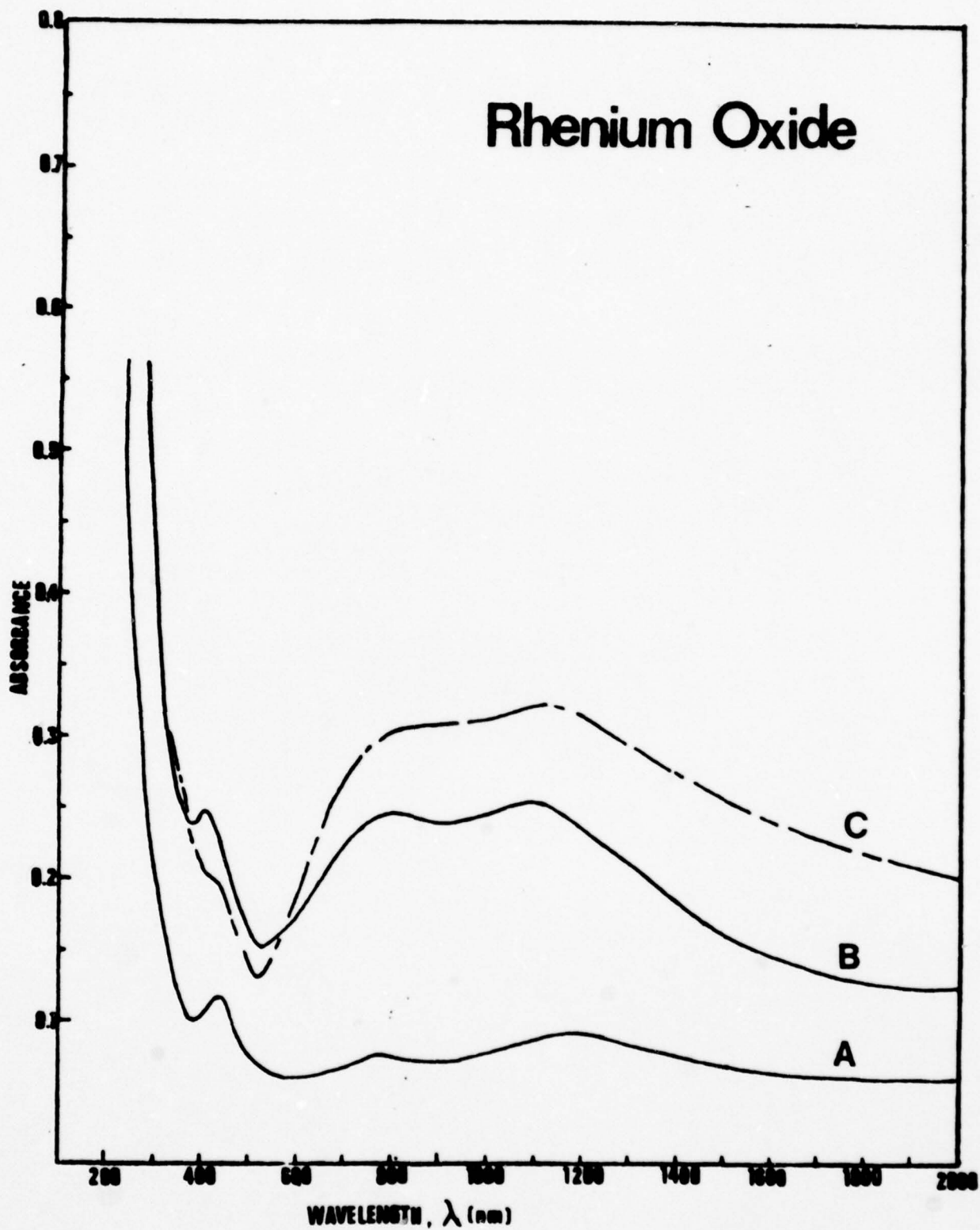


Figure 8. Absorbance spectra of Re_2O_7 (A) as-deposited and after heating in air at 150°C for (B) 0.5 min. and (C) 1 min.

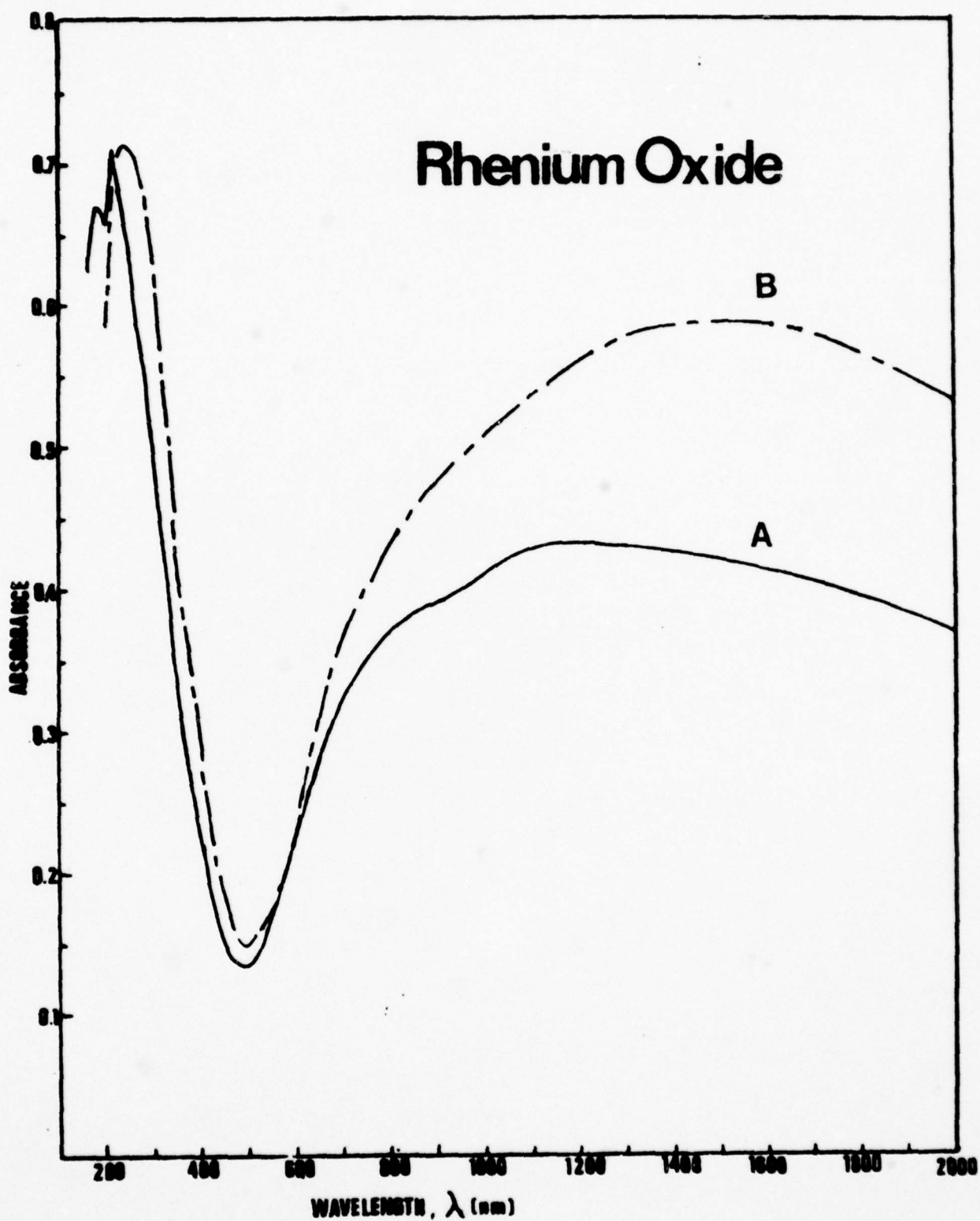


Figure 9. Absorbance spectra of Re_2O_7 after heating in air at 150°C for (A) 1.5 min. and (B) 2 min.

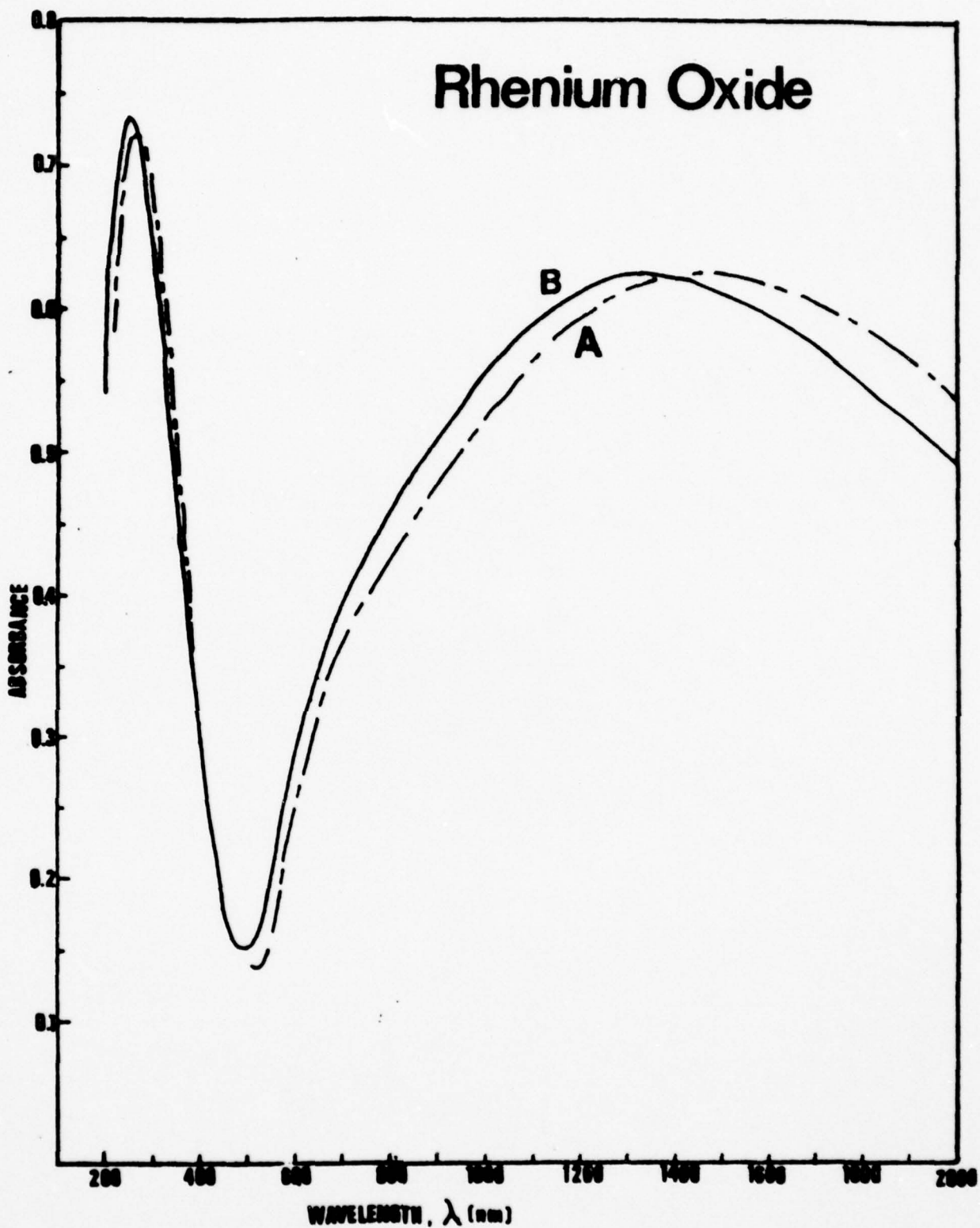


Figure 10. Absorbance spectra of Re_2O_7 after heating in air at 150°C for (A) 3 min. and (B) 11 min.

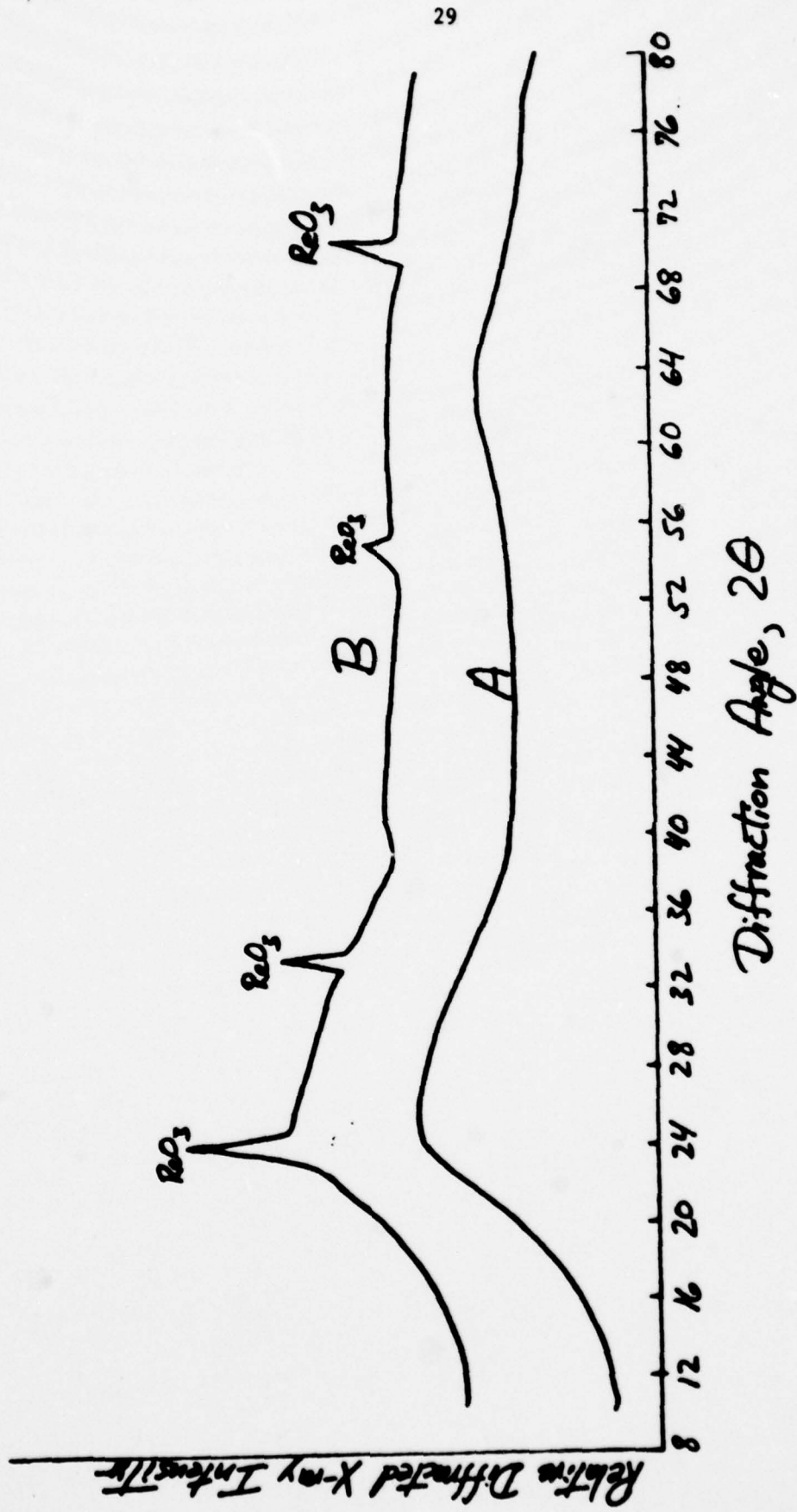


Figure 11. X-ray diffraction spectra of Re_2O_7 film on soda-silicate glass (A) as deposited and (B) after heat treatment at $150^\circ C$ for 2 min.

consistent with this finding. Figure 12 shows that the Re 4f spectrum of a TC-colored film contains features representing a combination of the features from both ReO_3 and Re_2O_7 . Thus the TC effects appear to be a result of a crystalline change in the thin films. The similarity of the TC and EC absorption spectra suggest that the origin of the EC effect may be of a similar nature.

(3) Electrochromic rate-controlling mechanisms in liquid electrolyte devices¹⁶

We have found that the application of a thin semi-transparent conducting layer to the WO_3 surface very markedly increases the rate of coloration that may be achieved.¹ The optical absorption of the conducting film was typically 5-10%. In addition, it has been found that the application of a small voltage to the conducting film, imposed in addition to the potential applied between the SnO_2 film and electrolyte, gives rise to a considerable increase in rate of coloration and bleaching.

The electrochemical cell in which the WO_3 film is placed in contact with 1 N H_2SO_4 has been shown in Fig. 1. Normally when the conducting layer was present, voltages were simultaneously applied to the SnO_2 layer, to the thin conducting surface layer, and to the counter electrode.

Figure 13 shows the change in optical transmission at 900 nm for a coloration and bleaching sequence obtained with 1.5 V applied between the SnO_2 and counter electrode. Curves a and b refer to a WO_3 film without and with a thin conducting surface layer respectively. Coloration proceeds rapidly when the SnO_2 layer is made negative relative to the electrolyte. Reversing the voltage gives rise to bleaching. Figure 13

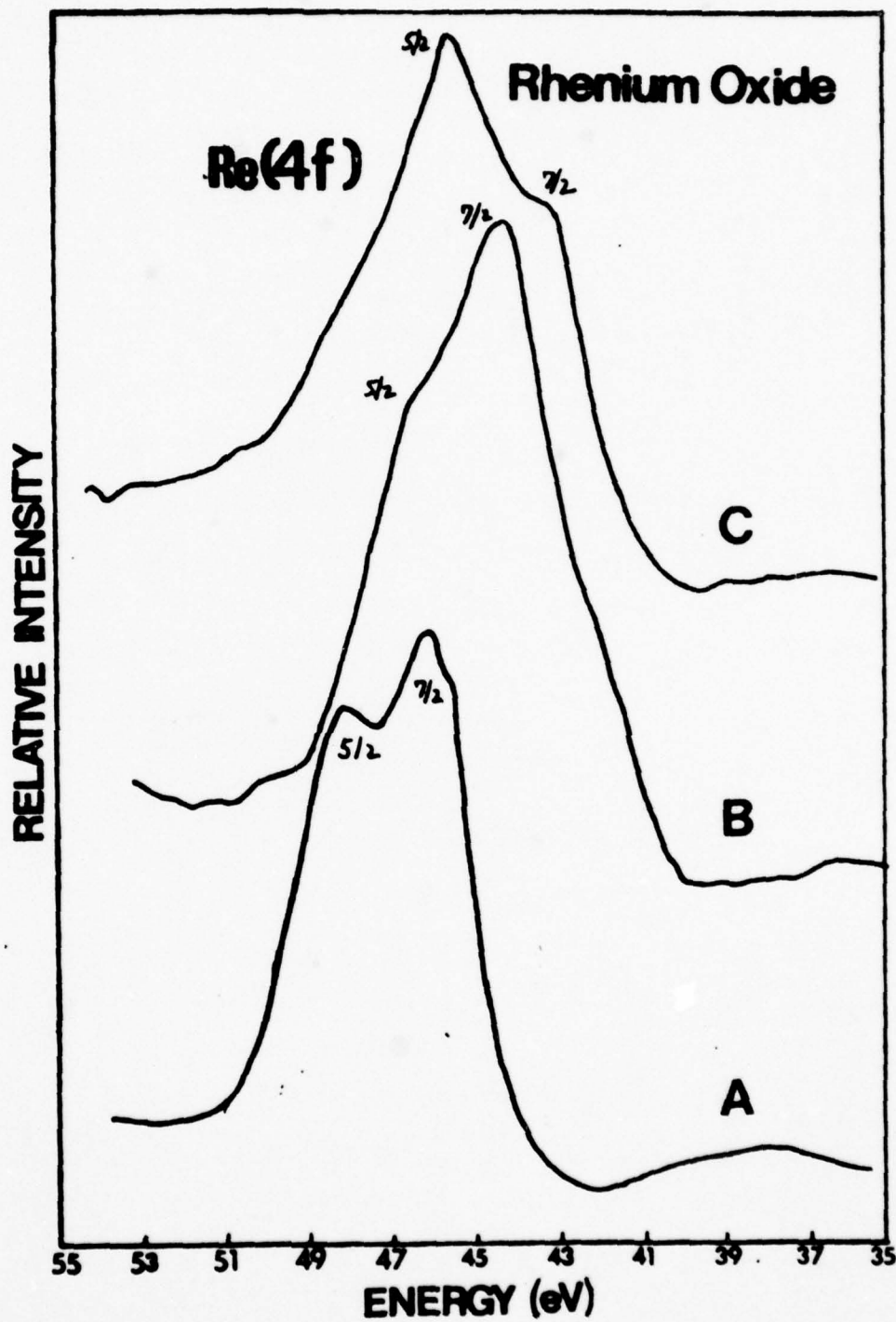
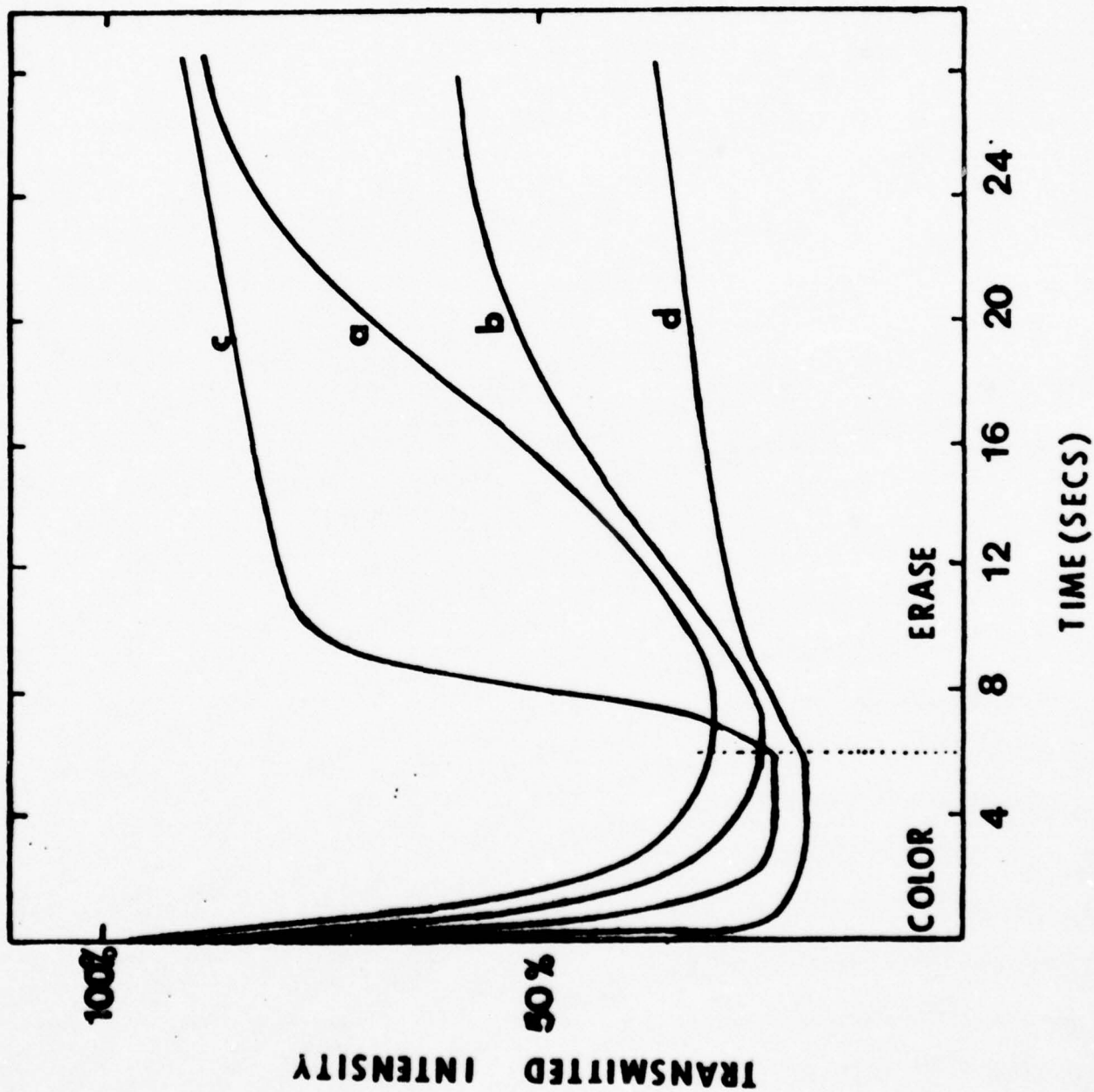


Figure 12. ESCA Re 4f core level spectra for (A) Re_2O_7 powder, (B) ReO_3 powder, and (C) a film vapor deposited from ReO_2 and colored by heating in air at 150°C for 0.5 min.

Figure 13. Change in optical transmission at 900 nm during a coloration and bleaching sequence. Curves (a) and (b) refer to WO_3 without and with a conducting overlayer, respectively. Curves (c) and (d) refer to WO_3 with +0.5 and -0.5 volts on the conducting surface layer with respect to the SnO_2 layer, in addition to 1.5 V between the SnO_2 and counter electrode.



shows that the presence of the conducting layer gave rise to a significant increase in the rate of coloration. Application of either +0.5 volts or -0.5 volts to the conducting layer electrode produced further increases in the rate of coloration, as shown in curves c and d. However, the application of +0.5 volts to the conducting layer gave rise to an increase in bleaching rate while a voltage of -0.5 V led to a large decrease in bleaching rate. With -0.5 V during coloration and +0.5 V during bleaching, very fast switching was observed (i.e. curves d and c were combined).

Coloration or bleaching could not be obtained by applying a potential between the SnO_2 layer and the gold layer when the connection between the SnO_2 layer and the counter electrode was removed. However, application of a voltage between the conducting layer and the counter electrode with the SnO_2 electrode disconnected was found to lead to coloration. Apparently electrons may enter the WO_3 from the conducting film to maintain charge balance when the protons enter the WO_3 film. Reversing the voltage however did not lead to substantial bleaching when the SnO_2 electrode was disconnected. The effect of the conducting film became much less marked as the film thickness was increased, probably because the porosity decreased and proton transport to the WO_3 film was blocked.

These results become understandable when it is realized that when the gold layer is not connected to an external voltage source, it attained a potential of approximately 1.2 volts relative to the SnO_2 film during coloration. While this affects the rate of C/B, it cannot explain the kinetics of the cells without the incorporation of a term accounting for resistance in the WO_3 and/or SnO_2 layer. In fact current/voltage measurements

indicate that this resistance has values of 100-200 Ω in cells without a conducting layer. With a conducting layer on the surface of WO_3 , the resistance was lower. A third consideration in writing equations to describe the kinetics of our electrochemical cell is that the equilibrium cell potential is a function of the composition of the WO_3 layer. As protons are injected into the film, the equilibrium potential shifts¹⁷ and this will affect the resulting kinetics. With these considerations we write the overpotential, η , as

$$\eta = E - E_e + j_p R_\Omega \quad (1)$$

where E is the potential applied, E_e is the equilibrium potential which varies with composition, j_p is the current, and R is the WO_3/SnO_2 resistance. Using the Butler-Volmer equation,¹⁸

$$j_p = j_o \left[\exp\left[\frac{(1-\alpha)e\eta}{kT}\right] - \exp\left[-\frac{\alpha e\eta}{kT}\right] \right] \quad (2)$$

where j_o is the exchange current density (assumed constant), α is the barrier symmetry factor, k = Boltzmann's constant, T is temperature, and e is the electronic charge. We can substitute η and reduce Eq. (2) to

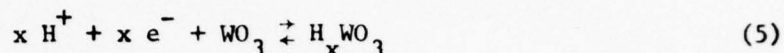
$$j_p = \frac{(E-E_e) [e/kt(E-E_e) + 1]}{P\sqrt{t} - R_\Omega [e/kT(E-E_e)+1]} \quad (3)$$

where

$$P = -\frac{RT\pi^{1/2}}{2F^2 c^* AD^{1/2}} \quad (4)$$

and R is the gas constant, F is the Helmholtz constant, c^* is the bulk

concentration, A is the area of the colored portion, D is the proton diffusion coefficient, and x is the number of electrons in the reaction



Equation (3) shows that if the resistance is high, the current is dominated by the term containing R_Ω and is independent of time. However, if the Helmholtz layer dominates, the kinetics are dependent upon $t^{-1/2}$. A plot of current versus $t^{-1/2}$ from the present cell is shown in Fig. 14. The current initially tends to be independent of time indicating resistance control. However at longer times, the kinetics become diffusion controlled and the current shows the $t^{-1/2}$ dependence.

This conclusion is supported by cyclic voltammetry measurements of which a typical example is shown in Fig. 15. In this technique the potential between the SnO_2 and Pt counter electrode was cyclically swept at various speeds, v (volts/sec). The data indicate that the peak current for bleaching obeys the $v^{1/2}$ law for both SnO_2/WO_3 and $\text{SnO}_2/\text{WO}_3/\text{conducting layer cells}$. This $v^{1/2}$ dependence has previously been ascribed to diffusion control across the Helmholtz layer,¹⁹ and is consistent with the conclusion that the Helmholtz layer may limit the rate of coloration (after a finite time) in EC devices. As might be expected based upon this hypothesis, the rate of coloration (i.e. the peak current increase) was higher for $\text{SnO}_2/\text{WO}_3/\text{conducting layer cells}$ versus SnO_2/WO_3 cells as shown in Fig. 15. In addition, data in Fig. 15 show that the coloration rate increased even further when the conducting layer was electrically shorted to the SnO_2 layer or when the conducting layer was at a negative

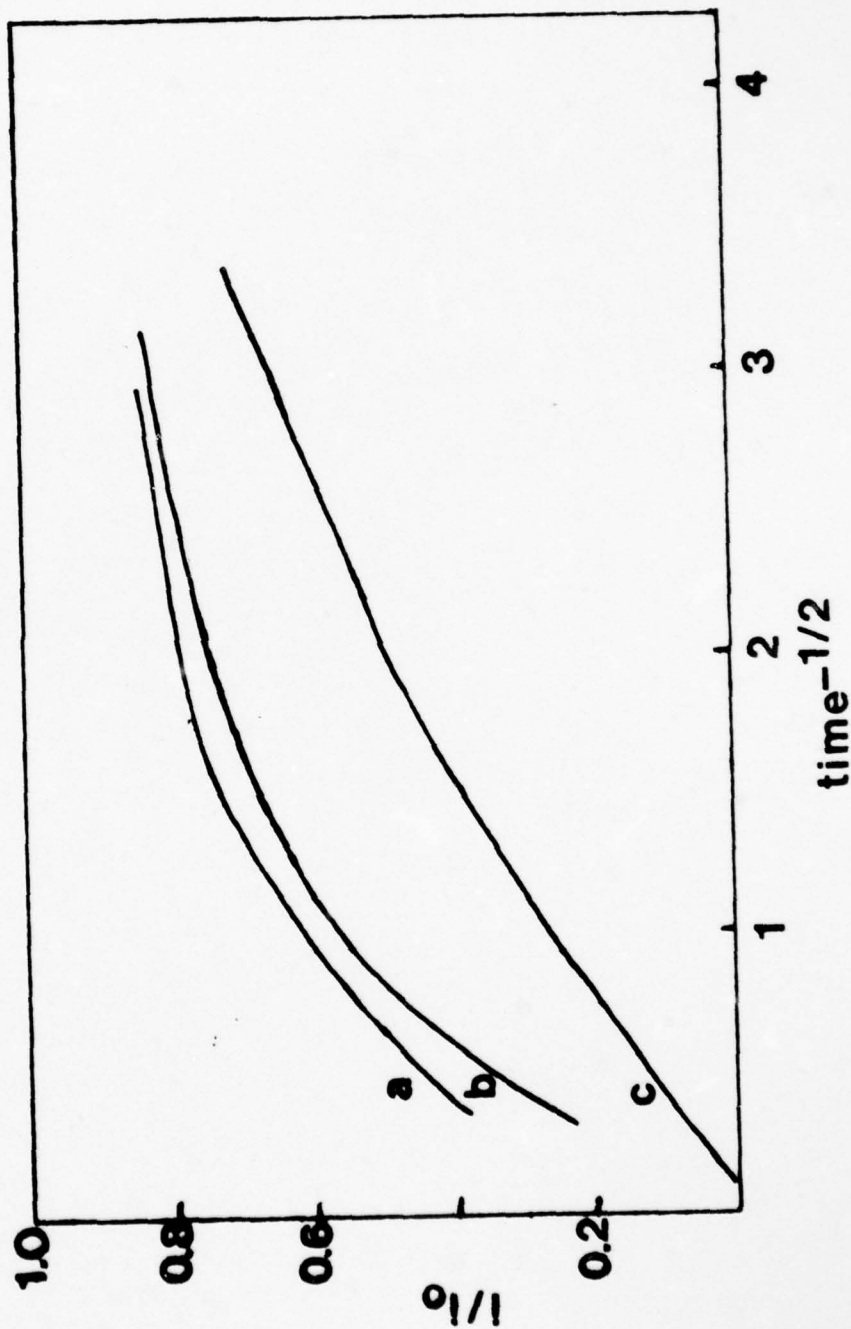
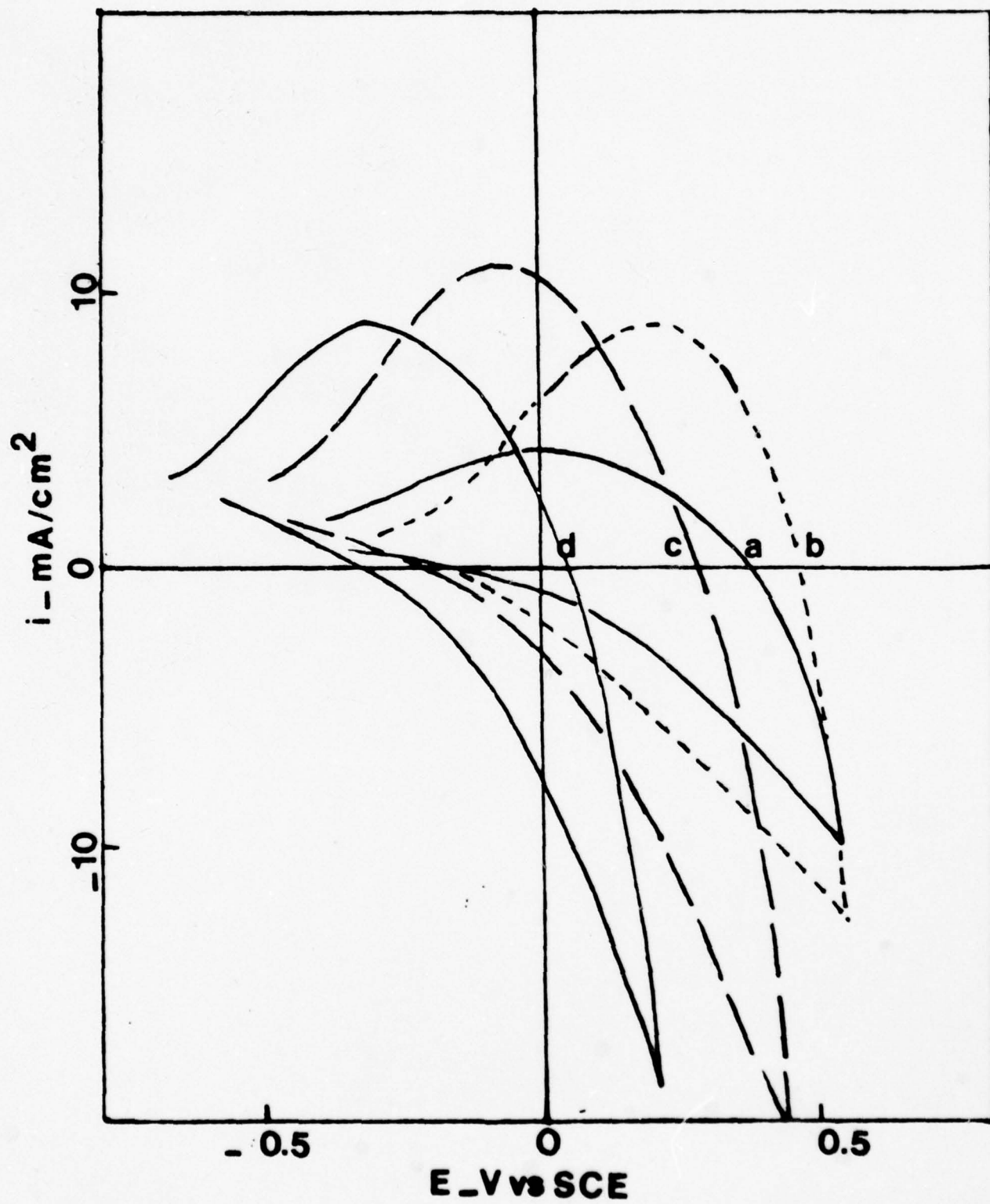


Figure 14. Current (I) changes with time during coloration normalized to the initial current (I_0) versus the inverse of the square root of time. Curves a, b, and c refer to +0.6, +0.4, and +0.1 volts respectively applied to SnO_2 and referenced to the calomel electrode.

Figure 15. Cyclic voltametry curves of current versus potentiostatic voltage reference to the calomel electrode. Curves a, b, c, and d refer to WO_3 , WO_3 with an electrically floating conducting layer, WO_3 with the conducting layer shorted to the SnO_2 layer, and with a potential of -0.1 volts applied to the conducting layer, respectively.



potential with respect to the SnO_2 .

Initially the coloration of WO_3 is not controlled by the Helmholtz layer and we have modelled this effect by adding a resistance term to the overpotential expression. However this effect could originate from resistance to injecting protons into the WO_3 films. To study this effect we have measured the flat band voltage for the devices in a photoelectrolysis experiment. A potentiostatic voltage was applied to the SnO_2 with respect to the Pt counter electrode and referenced to the calomel electrode. A mercury lamp was used to flood the cell with a spectrum of photons with good intensity at ~ 300 nm. A typical variation of photo current with voltage is shown in Fig. 16. The data show that the flat band voltages (the voltage necessary to compensate band bending at the surface) vary with the pH of the solution. The flat band voltage decreases as the pH increases and the slope is 0.059 mV/pH, which is similar to data reported by Bulter *et al.*²⁰ The WO_3 /conducting layer cells were found to have a lower flat band voltage in 0.5 N H_2SO_4 electrolyte (0.25 V) as compared to WO_3 cells (0.48 V), but in either case the flat band voltage decreased as pH increased. Data in Fig. 15 show that hydrogen was evolved at lower voltages with the conducting layer on the WO_3 , and this probably results from the effects of the conducting layer upon the flat band voltage. There is also evidence that the conducting layer increased the pH of the surface, probably by increasing the concentration of adsorbed protons on the surface.

Beyond investigating the rate of coloration versus sweep rate, the cyclic voltamogram in Fig. 17 demonstrates that H_2 is evolved in the

Figure 16. The variation of photocurrent with voltage applied to SnO_2 and referenced to the calomel electrode for (a) WO_3 on SnO_2 coated glass and for (b) WO_3 with a conducting layer in 0.5 N H_2SO_4 electrolyte.

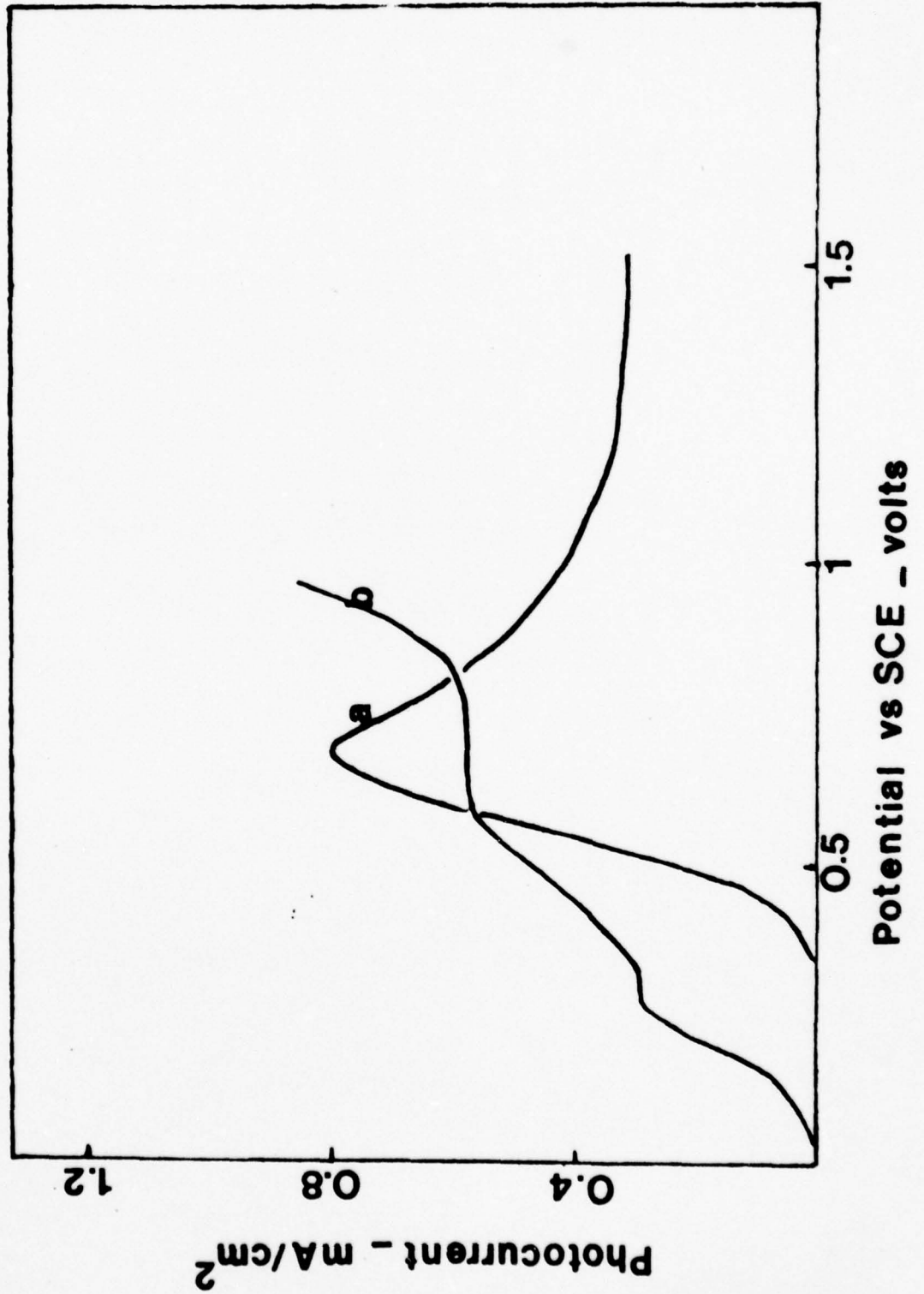
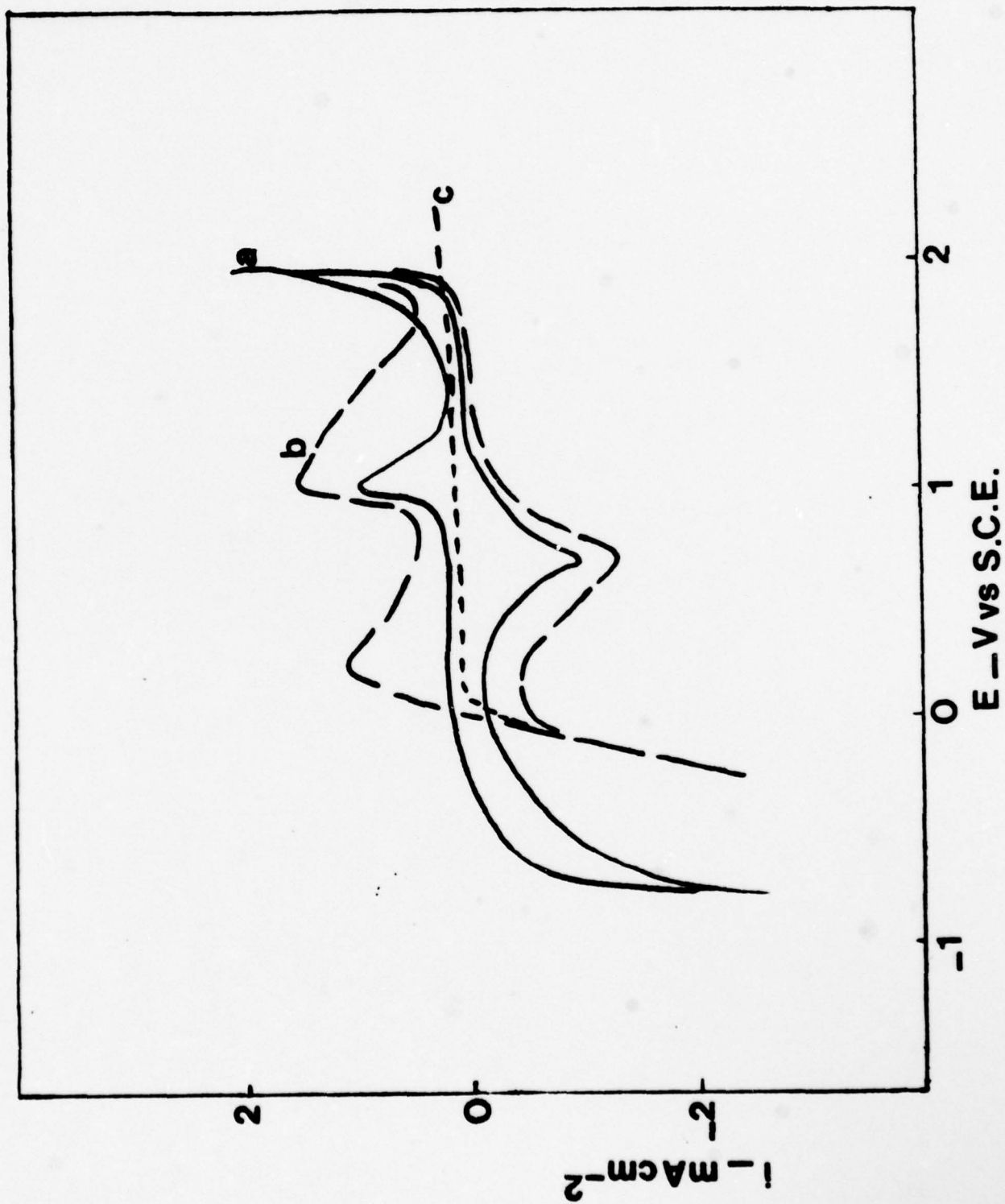


Figure 17. Cyclic voltammetry curves for (a) a conducting layer on glass, (b) a nonporous conducting layer on WO_3 , and (c) a porous conducting layer on WO_3 .



cathodic limit, and the current peaks at +1.1 and +0.8 volts represent oxidation and reduction, respectively, of the conducting layer. To study this effect further, conducting layers were deposited on glass substrates as well as on WO_3 on SnO_2 . The behavior of each of these types of samples was studied in electrochemical cells, as well as in composite cells where both substrates were incorporated simultaneously. The extent of oxidation and reduction of the conducting layer was substantial and similar on glass substrates and WO_3 substrates when the layer was continuous and nonporous. However upon cycling a few times between the anodic and cathodic limits, the conducting layer became porous, and the hydrogen evolution potential increased to a value between that for a uniform, nonporous conducting layer and for WO_3 surfaces. In this condition the conducting layer appeared resistant to oxidation and reduction as shown in Fig. 16. Some evidence for corrosion of the WO_3 itself was found, and the extent depended upon the history of the sample. The voltages at which WO_3 corrosion was significant were larger for films which had been heat treated for 60 min. at 250°C , however the depth of coloration was lower in these samples. As-deposited WO_3 displayed larger absorption coefficients, but the corrosion occurred at lower applied voltages.

The effects of the conducting layer porosity upon hydrogen evolution is similar in many respects to the results of Harris *et al.*²¹ for gold layers on GaP. They also found less corrosion of the overlayer for a porous film, yet their overlayer displayed blisters after ~ 100 cathodic-anodic cycles. Harris *et al.* controlled blistering by producing porosity

during deposition of the overlayer and by limiting the voltage extremes to below those at which gas was evolved. Similar characteristics in our films have been reported above.

Because of the patent being applied for,¹ the specific nature of the conducting layer has not been discussed in this report. A number of different materials were studied, and an optimized material and deposition technique has been selected. The University is currently discussing patent rights with various commercial companies.

(4) solid-state electrochromic devices

Solid-state cells were made using SiO and a proprietary solid state electrolyte (PSSE) as the source of positive ions. In the WO_3 -SiO cell, the injected ions are H^+ ions present in the SiO and WO_3 due to absorbed water vapor.²² The WO_3 could be colored and bleached as usual by application of a voltage. The rate of coloration was found to be much slower than that using an acid electrolyte, i.e. approximately 10 sec. being required to reach 10% absorption.

The PSSE electrolyte is a rapid proton conductor whose conductivity at room temperature has been found to be higher than that of $\beta-Al_2O_3$. PSSE was prepared by pressing it into pellets which were pressed against NESA glass with a deposited WO_3 film. The opposite side of the PSSE was either coated with Ag paste or pressed against another NESA glass plate. For better adhesion and uniform surface contact to WO_3 films, the pressed pellets were coated with a thin layer of PSSE paste. The paste was made using less than 1% by volume of 1 N H_2SO_4 . This structure was dried in water-rich atmospheres at 50-80°C for 1/2 h. The speed of coloration

and bleaching with this electrolyte was comparable to that of dilute H_2SO_4 as an electrolyte. As shown in Table 1, this method results in a reflectivity difference of 36% after 0.7 sec. at 5 mA. Here reflectivity difference is defined as $(R_1 - R)/R_1 \times 100\%$, where R_1 and R are the initial and instantaneous reflected light intensities. However, high applied voltages were required to reach the same degree of coloration as compared to H_2SO_4 , due to resistance of the 1 mm thick electrolyte. This resistance can be decreased by using more dense and thinner electrolyte pellets.

PSEE was successfully applied as a paste, in addition to the above technique. In one method, PSSE paste was made using a binder, e.g. potassium silicate. This paste was applied to the WO_3 -coated NESA glasses by a doctor-blading technique. Silver paste was used as a counter electrode. This was dried in the same manner as above. In a second procedure, pastes were made by dissolving PSSE in dilute H_2SO_4 , reprecipitating with NaOH and filtering. This gave a very fine particle size. Tungsten trioxide-coated NESA glass was coated with this paste, then dried as above. Similar PSSE pastes were also used in cells as a liquid electrolyte for electrochromic coloration. In all preparation the electrochromic response time was faster than that reported by Green *et al.*²³ for $\beta-Al_2O_3$ electrolytes (see Table 1).

In all devices except those with high density pellets, PSSE was opaque and colored yellow, which contrasted well with the blue electrochromic color. High density pellets developed a translucent character which would allow its use as a backlighted display. PSSE is also insoluble in water and is stable up to 80°C in atmosphere. Although lifetime data

Table 1: Electrochromic Response versus Electrolyte type and Electrolyte Treatment

Material	Treatment	Thickness of the Electrolyte		Current Applied (Volts)	Voltage Applied (Volts)	Reflection Contract	Response Time
		Electrolyte	mA				
1. Dilute H_2SO_4		-	5	0.6	0.6	36%	0.6 sec
2. PSSE Pellet Dried at 80°C Dried at 50°C		1 mm	5	15	1.0	36%	1.0 sec
		1 mm	5	5-8	0.7	36%	0.7 sec
3. PSSE Paste With potassium silicate binder (dry) Reprecipitated from dilute H_2SO_4 solution	i. Dry	0.5 mm	3	20	5.0	36%	5.0 sec
	ii. Wet (slightly acidic)	0.5 mm	4	15	2.0	36%	2.0 sec
		1 mm	5	1-2	0.7	36%	0.7 sec
4. $\beta-Al_2O_3$			0.3		10	~30%	sec

are very sparse, no degradation of WO_3 films was observed in devices operated at low voltages. Upon coloring and opening the electrical circuit, some of the devices showed a decrease in reflectivity difference of about 5%. A 100 Å layer of SiO₂ deposited on the WO_3 films reduced this open circuit change in reflection contrast. A patent disclosure has been filed to protect the University's rights to this discovery.

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Appendix 1
"Electrochromism in WO_3 Films with BaO Additions"

Electrochromism in WO₃ films with BaO additions

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Films of WO₃ with various amounts of BaO additions were deposited from multiple evaporation sources onto glass substrates heated to 100°C. The atomic percent of Ba in each film with respect to W was determined using particle-induced x-ray emission analysis (PIXIE). Compositional variations with film depth were examined using Auger electron spectroscopy combined with ion beam milling. The electrochromic coloration and decoloration behavior was measured in an electrochemical cell. It was found that additions of Ba as small as 10 at. % measurably reduced the amount of coloration induced per given amount of charge injected into the film. The amount of inhibition of electrochromic coloration was found to increase with increasing Ba concentration. At Ba concentrations greater than 45% the coloration effect was virtually eliminated. Ba additions greater than 45 at. % were also found to induce crystallization in the films.

PACS numbers: 82.45.+z, 78.20.Jq, 61.70.Dx

I. INTRODUCTION

The phenomenon of electrochromism—the inducement of a reversible color change in a material by the application of a small dc voltage—has received considerable attention during recent years due to the potential application of this effect to electrically alterable, low-power displays suitable for high light ambient and having inherent memory. Most of the published research in inorganic electrochromics has been directed to understanding the effect as exhibited in amorphous thin films of WO₃, which electrochromically switch from transparent to deep blue.¹⁻⁷ Coloration is brought about by the simultaneous injection of electrons and positive ions (most commonly H⁺ ions) induced by the application of a small dc voltage (typically 1.5 V) across the film. The electron-injecting contact is commonly a transparent conductive coating on a glass substrate, while the proton injecting contact is usually a dilute H₂SO₄ solution into which an In or Pt electrode is inserted. The injected charge gives rise to a broad absorption band with a maximum at ~1.38 eV.⁶ Reversing the polarity of the applied voltage results in decoloration. It should be noted that WO₃ is also photochromic; i.e., blue coloration can also be induced by ultraviolet irradiation.¹

The precise electronic mechanism of EC absorption in WO₃ has not been conclusively established. Hollinger *et al.*⁶ have proposed that during the electron injection an increase in the number of localized W⁵⁺ states situated ~2 eV above the valence-band edge occurs. These states may give rise to small polaron formation. The absorption results from small polaron transfer⁷ or intervalence charge transfer³ when electrons are excited between W⁵⁺ and W⁶⁺ ions.

One useful experimental approach to the clarification of the absorption mechanism is to study the effect of the addition of various metal-oxide ions on the EC behavior. Ionic additions could for example alter the transition-metal ion site separation and thereby alter the energy at which the absorption maximum occurs. The presence of other transition metal ions could also serve as additional receptors and sup-

pliers of electrons during the excitation process. Faughnan⁸ has examined films made by coevaporating WO₃ and MoO₃ (which is also known to be electrochromic).⁹ He found that Mo additions cause an increase in the energy of the absorption band maximum, the largest increase being for an addition of 7% MoO₃ ($E_{max} = 2.05$ eV). Faughnan used his results to argue in favor of an intervalency transfer model.

In the research discussed in the present paper we have studied the effect of the addition of various amounts of BaO to WO₃. One stimulus for the examination of the WO₃/BaO system was the observation by Sakka¹⁰ of photochromic switching of BaWO₄:Bi(0.1 mol %) powder from white to red. It was thought that the incorporation of BaO in WO₃ films may give rise to interesting results in the EC absorption process.

II. EXPERIMENTAL PROCEDURE

Mixed-oxide films of WO₃/BaO of various compositions were deposited on glass substrates, some of which were coated with conducting SnO₂, by coevaporating WO₃ and BaO powder. The WO₃ was evaporated from an alumina-coated tungsten crucible and the BaO was evaporated from a tantalum boat. During deposition the substrate temperature was 100°C and the pressure in the vacuum chamber was 4×10^{-6} Torr (5.3×10^{-4} Pa). The average total deposition rate as determined by a quartz crystal monitor was 20 Å/s and the film thicknesses ranged from 0.20 to 0.40 μm.

The atomic percent of Ba with respect to W in each film was determined by PIXIE (particle-induced x-ray emission) analysis.^{11,12} Barium additions ranging from 10% to 100% (100% representing pure BaO) were studied. Auger electron spectroscopy equipped with ion milling capability was used to investigate any compositional variations with depth in the film. An x-ray diffraction scan was also made on each film to determine whether or not the film was amorphous. The EC response of each film was studied using the electrochemical cell represented in Fig. 1. A dc potential of 1.5 V was applied

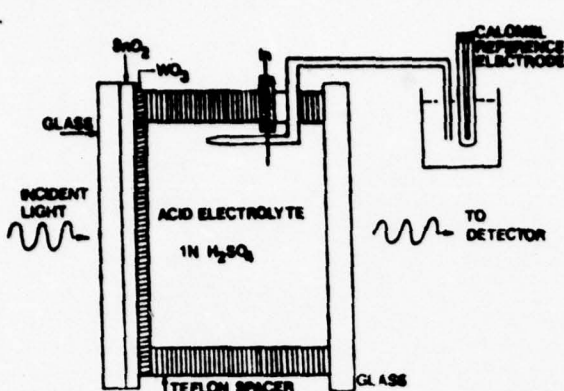


Fig. 1. Schematic of the electrochemical cell used to electrochemically induce coloration and decoloration in WO_3/BaO thin films.

across the SnO_2 and In electrodes. The In electrode was immersed in a 1N H_2SO_4 solution. The transmitted intensity of an incident monochromatic beam of red light (1.80 eV) was measured as a function of coloration and decoloration time. A representative curve for WO_3 and for $WO_3:Ba$ (10%) is shown in Fig. 2(a). The current through each film during coloration and decoloration was also measured as shown in Fig. 2(b).

III. EXPERIMENTAL RESULTS AND DISCUSSION

Addition of BaO to films of WO_3 was found to have an inhibiting effect on their coloration ability. For example, Fig.

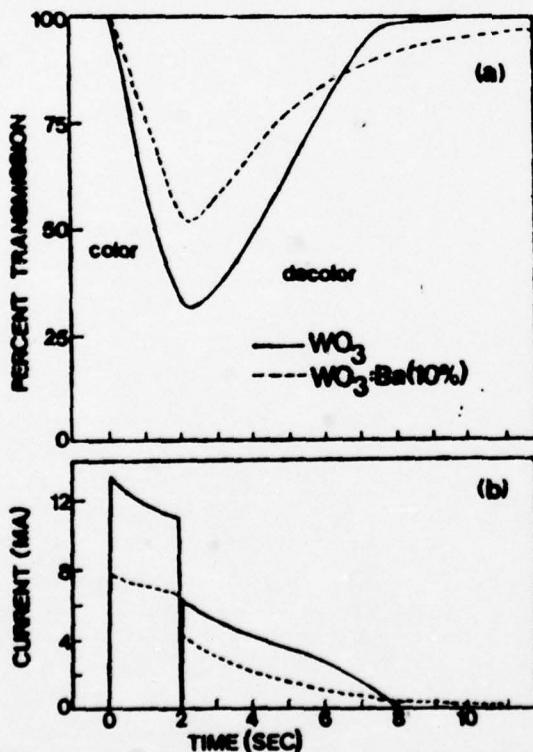


Fig. 2. (a) Percent transmission of monochromatic red light (1.80 eV) through a WO_3 and a $WO_3:Ba$ (10%) film, respectively, as a function of coloration and decoloration time for 1.5 V applied across the SnO_2 and In electrodes. (b) corresponding variation of current through the respective film during coloration and decoloration.

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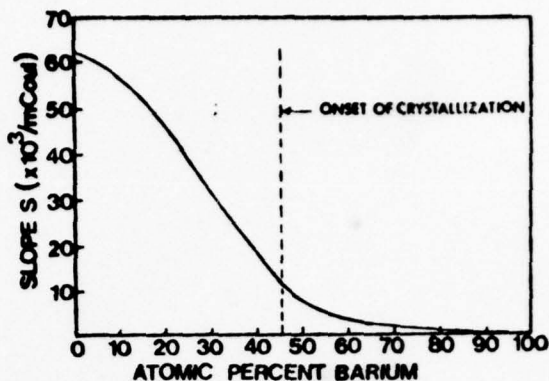


Fig. 3. Variation of slope S of $\ln(I_0/I)_t$ vs $(\int dt)_t$ with Ba concentration in WO_3/BaO films. S is a measure of the amount of coloration induced for a given amount of charge injected.

2(a) shows that addition of 10% Ba reduces the total amount of light absorbed electrochromically in comparison to pure WO_3 . A measure of the amount of coloration induced for a given amount of charge injected is given by the slope S of a plot in $\ln(I_0/I)_t$ vs $(\int dt)_t$, where $(I_0/I)_t$ is the ratio of incident light intensity to transmitted light intensity after coloration time t and $(\int dt)_t$ is the area under the current-time curve after time t . The variation of S with Ba concentration is shown in Fig. 3. It is seen that the ability to inhibit coloration increases with increasing Ba concentration. For Ba concentrations up to 10% the coloration inhibition is small. For Ba concentrations greater than 40%, however, the inhibition is almost total. The form of the S -vs-concentration plot was not found to vary significantly with wavelength of the incident light in the range 1.1–1.8 eV. It should be noted that those films with ~10% Ba were found to have a deep blue coloration upon removal from the vacuum system. This coloration was removed by application of a decoloration potential of 1.5 V. Such coloration in the virgin condition was not observed in any of the pure WO_3 film or in films with Ba concentrations much greater than 10%. Sharp peaks were found to emerge in the diffuse x-ray diffraction patterns of the films at Ba concentrations greater than ~45%, indicating the onset of crystallization. The amount of crystallization was found to increase with increasing Ba concentration. It is believed that the presence of crystallites is at least partly responsible for the coloration inhibition in these films with the higher Ba concentrations. Further experimental work is necessary for the elucidation of the coloration inhibition at lower Ba concentrations. One possible explanation, however, is that the Ba addition increases the tungsten ion site separations sufficiently to decrease the probability of optically induced excitation between these ions. Auger electron spectra obtained for selected films indicated that the tungsten, barium, and oxygen concentrations did not vary significantly with depth into the films.

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- ¹¹A forthcoming paper will deal with the application of PIXIE to the analysis of thin films of WO_3 with various additives.
- ¹²For a set of recent papers on PIXIE see the "Proceeding of the First International Conference on PIXIE Analysis", *Nucl. Instrum. Methods* **148**, 1 (1977).

Appendix 2
Project Personnel

Dr. Derek B. Dove served as the project's Principal Investigator until he left the University of Florida for IBM, Yorktown Heights, NY, in August 1977. Since that time, Dr. Rolf E. Hummel has been directing this research as a principal investigator.

Dr. Hummel has had experience with optical and electrical properties of metals and alloys since 1958. He has developed, at the University of Florida, the differential reflectometer, which has been used for this research and which is capable of precisely measuring the transmissivity and reflectivity of electrochromic devices. Dr. Hummel is the author of a book entitled Optical Properties of Metals and Alloys, which was published in 1971 in the series *Reine Und angewandte Metallkunde in Einzeldarstellungen* (monographs in Pure and Applied Metallurgy) by the Springer Publishing Company. Dr. Hummel teaches courses in optical properties of metals, electron theory of metals, and electrical and magnetic properties of metals and semiconductors. Professor Hummel also has experience in thin film technology through his project on "Electrotransport in Thin Films," which has been supported for ten years by NASA and the Air Force.

Dr. Holloway has served as a co-principal investigator on the project since August 1978. He has worked with the physical and chemical properties of surfaces and thin films since 1969. His work has emphasized the study of these properties using materials characterization techniques

involving electrons in both core and valence levels. He is the author of 45 publications and reports related to his past activities. He is currently directing research on the effects of composition and structure upon the efficiency of polycrystalline silicon photovoltaic devices. This detailed correlation between composition, microstructure, and electrical properties is very complementary to this research project.

Two graduate students have been working on this project, Mr. A. R. Haranahalli and Mr. B. Molnar. This research will form the basis for their doctoral dissertations. Mr. Haranahalli will graduate in March 1980, and Mr. Molnar, who has worked on the project for the past three years, is expected to graduate with a Ph.D. in August 1979.

Appendix 3
Publications and Presentations

Publications

B. J. Molnar, A. R. Haranahalli, and D. B. Dove, "Electrochromism in WO_3 Films with BaO Additions," J. Vac. Sci. Technol. 15, 261 (1978).

Presentations

- * B. J. Molnar and D. B. Dove, "Electrochromism in WO_3 Films," 19th Electronic Materials Conference (AIME), June 1977, Ithaca, NY.
- * B. J. Molnar and D. B. Dove, "Electrochromism in WO_3 Films with Atomic Additions," 24th National Symposium of the American Vacuum Society, November 1977, Boston, MA.
- * A. R. Haranahalli, P. H. Holloway, and D. B. Dove, "The Influence of Metal Overlayers on Electrochromic Behavior of WO_3 Films," 21st Electronic Materials Conference (AIME), June 1979, Boulder, CO.