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REFLECTANCE MODULATION WITH ELECTROCHROMIC Li_xWO_3 FILMS

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Abstract

Reflectance-modulated Smart Glass[1] Windows (or smart windows) is a potentially important application for electrochromic thin films. The question addressed in this paper is, what is the upper bound for the near infrared reflectivity modulation in Li_xWO_3 films? Based upon recent research on bulk crystals of Na_xWO_3 and bulk crystals and thin films of polycrystalline Li_xWO_3, it is concluded that the upper bound is probably close to that of bulk crystals of Na_xWO_3 ($x>0.5$) for which near infrared reflectance > 90% has been reported.

Introduction

Controlled radiant energy transfer through windows can lead to important energy savings by decreasing heating and cooling loads and by reducing electrical lighting requirements in buildings; as well as by reducing cooling loads in vehicles. Electrochromic smart windows are very attractive candidates for achieving such controlled energy transfer since they can potentially provide electrically-controlled spectrally-selective optical transmittance modulation with only a modest expenditure of electrical energy to effect the modulation. We have previously proposed [1] a completely inorganic solid state electrochemically balanced 5-layer structure (Fig. 1) for such a window and have reported on the successful fabrication and evaluation of small area prototypes (< 20 cm^2). The five layers include two transparent (electronic-) conducting (TC) layers which sandwich a (mixed electronic/ionic conducting) electrochromic (EC) layer that is separated from a (mixed electronic/ionic conducting) counterelectrode (CE) layer by an (electronic insulating) ionic conductor (IC) layer. By double injection or extraction of electrons (from the TC layers) and charge compensating ions (from the CE layer) the transmittance of the EC layer can be selectively altered over the solar spectrum, since the change in free electron population modulates the transmittance.

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[1] Smart Glass is a trademark of Smart Glass, Inc.

DISCLAIMER

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APPENDIX A

["Reflectance Modulation with Electrochromic Li_xWO_3 Films," (invited paper), Proc. Electrochemical Society Conference on electrochromic Materials, Hollywood, Fla (Oct.1989).]

Ideally, to avoid unnecessary absorption, which can lead to long term degradation as well as thermal radiation transfer inefficiencies, the EC layer in an electrochromic window should have a spectral reflectance which is a step-function. Below a critical wavelength, λ_p, the reflectance should be zero (100% transmittance), and above λ_p the reflectance should be 100% (zero transmittance), and λ_p should be controllable. An ideal free electron (Drude) solid with no damping (no electron scattering) would exhibit the desired reflectance step function, with λ_p corresponding to the plasma wavelength. That is, $\lambda_p = (2\pi \cdot c)/\omega_p)$, (c = vacuum velocity of light, $\omega_p^2 = ([n_e]\, q^2/m^*\, \varepsilon_o)$, $[n_e]$ = density of free electrons, q = electronic charge, m^* = electron effective mass, ε_o = vacuum dielectric constant). Therefore, for the ideal Drude solid, a step-like spectrally selective reflectance modulation can be accomplished by modulating the free electron density. In any real film, however, there is some free electron scattering. This is introduced into the Drude model by the use of the damping or energy loss parameter, E_Γ, which largely determines the shape and height of the reflectance step [2]. Also, for films, as E_Γ is reduced, the required film thickness to attain a desired reflectance is likewise reduced. This can strongly affect the economics as well as the physical properties of smart windows. In particular, reduced thickness translates into diminished materials and fabrication costs, and shorter switching time; and, finally, reduced E_Γ and thickness translate together into significantly reduced heating from optical absorption (recall that optical absorption is a function of the <u>product</u> of the thickness and absorption coefficient). Therefore, being able to identify the causes of E_Γ and removing them, is both an interesting scientific challenge as well as of technological importance.

The purpose of this paper is to present evidence for the argument that the potentially achievable reflectance for Li_xWO_3 films can approximate that reported for Na_xWO_3 bulk crystals - i.e., E_Γ in Li_xWO_3 films can approach values close to those found for bulk crystals of Na_xWO_3 (in which $E_\Gamma < 0.25$ eV, when $x > 0.5$, has been reported [3]).

Current Studies

In our current studies we have been investigating bulk crystals of Na_xWO_3 and Li_xWO_3 that have been electrochemically grown, and polycrystalline (pc) films of WO_3, that have been rf-sputter deposited, and lithiated after deposition.

Growth and Measurements of Bulk Crystals of Sodium and Lithium Bronzes:

Na_xWO_3 and Li_xWO_3 bulk crystals (< 2mm x 2mm in cross-section area) were grown by a standard cathodic electrochemical growth technique [4], using molten solutions of M_2WO_4 (M = Li, Na) and WO_3 in various molar ratios.

Selected crystals were subsequently polished optically flat (optical flatness was checked using a HeNe laser, and the surface of some samples were examined with an SEM). Because the area of the samples were generally too small to be measured with a standard laboratory optical spectrophotometer, we assembled a microscope/monochromator system which employed focusing optics such that the illuminated area on the samples was smaller than the sample area itself. The optics were carefully adjusted to insure that all reflected photons were collected by the microscope objective. A calibrated aluminum mirror was used as a reference.

For the near infrared a lead sulfide detector was used and for the visible a silicon detector was utilized.

Shown in Figs. 2 and 3 are typical measured reflectances for bulk crystals of Na_xWO_3, and bulk crystals of Li_xWO_3, respectively. For these two curves, Drude model fits were made, using $\varepsilon_b = 4$ and assuming a fixed effective mass $m^* = 0.5\ m_o$ (m_o = free electron mass). These fits yielded the pairs of Drude parameters: [E_p (the unscreened plasma energy), and E_Γ (the energy loss parameter)]; and the pairs are indicated in the figure captions.

Preparation and Measurements of pc-WO_3 films:

pc-WO_3 films were prepared by an rf-sputter deposition process, using: a 5-inch target of (partially-reduced WO_3 - obtained from Cerac, Inc.), 200 Watts of rf power (13.5 MHz), and for the samples whose results are shown in Fig. 4, an atmosphere of 2 mTorr oxygen and 4 mTorr argon was used. A target-substrate distance of 7.5 cm was generally employed, and the substrate (soda-lime glass) temperature was approximately 430 - 440 °C. The film thicknesses were approximately 200 nm, and the films were lithiated after deposition, using either an electrochemical technique (1M lithium perchlorate in propylene carbonate as the electrolyte, platinum or carbon as the counter electrode) or by a vacuum sputter-deposition technique. For all the samples, (bulk crystal and films) X-ray analysis and atomic absorption spectroscopy are being employed to determine the lithium content; these studies are underway and will be reported subsequently. The spectral reflectance of two pc-Li_xWO_3 films are shown in Fig. 4. A Drude model fit, using $\varepsilon_b = 4$, and $m^* = 0.5\ m_o$, yielded the [E_p, E_Γ] pairs: (a) [3.43 eV, 0.59 eV]; and (b) [3.50 eV, 0.42 eV]. The spectral reflectance was measured by using a spectral reflectance attachment with a Beckman DK-1 spectrophotometer. The angle of incidence was < 20° from the normal.

Analysis and Results

In the absence of accurate measurements for the lithium concentrations (x) of our samples, we have resorted to using the fitted (unscreened) plasma energy, E_p, to estimate x. We then plotted E_Γ as a function of $(E_p)^2$, as shown in Fig. 5. [We have used $(E_p)^2$ because it is proportional to the free electron concentration.] Also shown in Fig. 5 are data obtained from Owen et. al. [3] for Na_xWO_3 bulk crystals. The following observations may be noted.

1. The data for E_Γ for three Li_xWO_3 crystals linearly extrapolate to values of E_Γ less than that observed for the Na_xWO_3 crystals.

2. The intersection of the linearly extrapolated E_Γ plots for the lithium bronze crystals and for the sodium bronze crystals of Owen et.al.is at a value of $(E_p)^2$, [approximately 14 $(eV)^2$], which we estimate would correspond to an x-value of approximately 0.5, (using the data of Owen et. al. to obtain x, as discussed further below).

3. There is one Li_xWO_3 film for which E_Γ (0.42 eV) is comparable to that found for a Li_xWO_3 crystal of similar $(E_p)^2$, (or similar x-value).

4. There is one Na_xWO_3 crystal which exhibits a higher E_Γ and one that exhibits a lower E_Γ than for the Na_xWO_3 crystals investigated by Owen et. al. Furthermore, surface color variations were observed by eye for the Tufts sodium bronze crystal with a higher E_Γ, indicating that the crystal was inhomogeneous.

5. The 80% infrared reflectance shown in Fig. 4 for a Li_xWO_3 film is the highest yet to be reported for intercalated WO_3 films. This demonstrates that the lower reflectances previously observed were not intrinsic limits.

6. An estimate for the x-values was obtained by using the data reported by Owen et. al. for Na_xWO_3, for which the x-values were found by X-ray measurements. In particular, we assumed the bound dielectric coefficient (ε_b) to be fixed at 4, and we obtained E_p by using the relationship: $E_p = (\varepsilon_b)^{1/2}(E_p)_{screened}$, where $(E_p)_{screened}$ is the photon energy at which the real part of the complex dielectric response function is zero. In this manner we obtained an estimate for $(E_p)^2$ vs. x, which is plotted in Fig. 6. From this figure we estimate that the maximum achievable range for E_p is approximately 4.0 - 4.5 eV (corresponding to $[(E_p)_{screened}]_{max} = 2.0$ - 2.25 eV. The basis of this estimate is the theoretical maximum value for x (for reversible lithium insertion in WO_3), which is 0.75, and the empirically observed maximum value for x which is in the range of 0.6 - 0.75.

Further Discussion and Conclusions

The results reported above suggest that there should be little inherent difference between the infrared reflectances of lithium and sodium tungsten trioxide for x-values > 0.5. This conclusion is based on the following reasoning.

1. Both bronzes exhibit cubic symmetry for x > 0.5, albeit for different space groups.

2. Previously reported research has shown that extended defects are the principal source of electron scattering [7], and such defects occur primarily because of oxygen nonstoichiometry and other possible growth-induced disorder.

3. Previously reported research on films of Li_xWO_3 [8], consistent with the results reported above, has shown that increased alkali concentration results in decreased electron scattering (decreased E_Γ), probably as a consequence of the known ordering of the alkali atoms [6].

4. The spread for E_Γ among different crystals of nearly the same average alkali concentration (and for the same alkali atom) is approximately the same as that seen between crystals of different alkali atoms (cf Fig. 5). It is highly likely that the concentration and distribution of growth-induced defects (e.g., oxygen nonstoichiometry, stacking faults, clustering, nonuniform distribution of alkali ions, etc.) can lead to variations between the optical properties of independently prepared samples.

5. There has been a steady improvement in the reported values of the near infrared reflectance for pc-M_xWO_3 films (M = H or Li) from approximately 35% in 1977 [9] to the 80% reported in this paper; and our current results have shown that E_Γ can be reduced to a value no more than a factor of 2 higher than that which has been obtained for Na_xWO_3 crystals.

Thus, we summarize our conclusions as follows. For the same x-values, both films as well as crystals of Li_xWO_3 can probably be prepared which will exhibit reflectances approximately as high as the highest that have been obtained for Na_xWO_3 crystals; and, in particular, $E_\Gamma < 0.25$ eV should be attainable for pc-Li_xWO_3 films having $x > 0.5$. With such low E_Γ the films would have near infrared reflectances > 85%, and would have a very positive impact on the development of high performance electrochromic windows.

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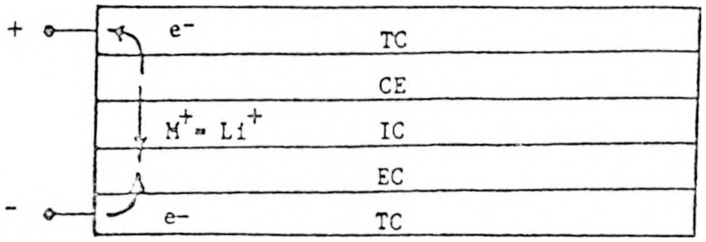

Figure 1. An electrochromic smart window structure: TC = transparent conducting layer, CE = counterelectrode layer, IC = ion conducting layer, EC = electrochromic layer. Polarity is shown for cathodic coloring.

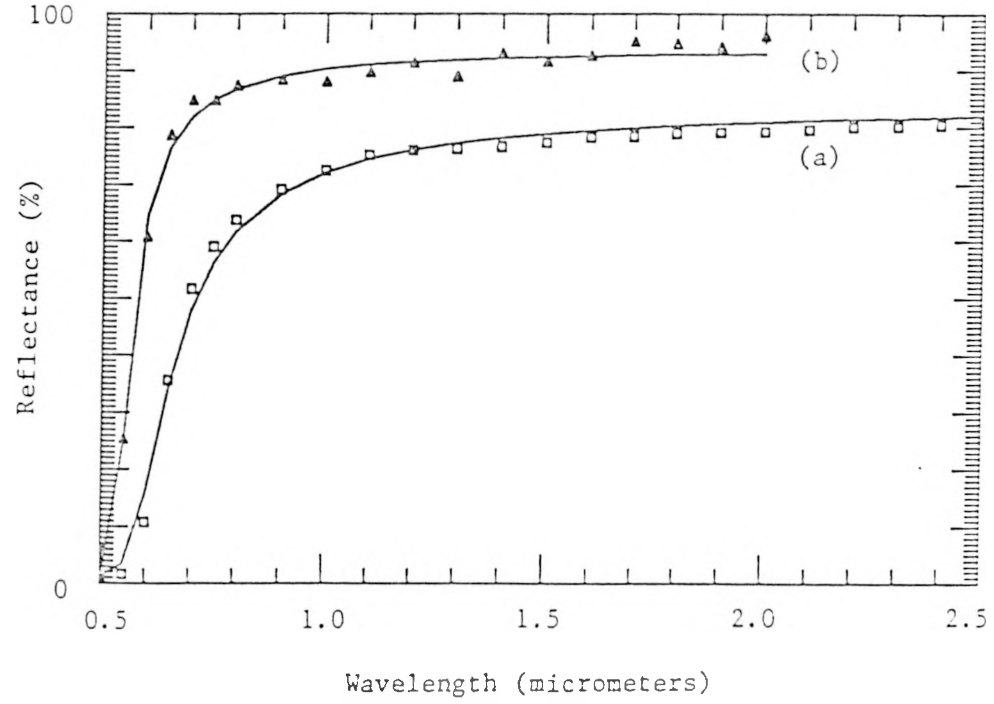

Figure 2. Reflectivity wavelength dependence for two crystals of Na_xWO_3. {(a) = crystal melt had a [Na]:[W] ratio of 1.4 - crystal kindly supplied by A. Wold; (b) = crystal melt had a [Na]:[W] ratio of 0.94.} Pairs of Drude model parameters, [E_p (the unscreened plasma energy), and E_Γ (the energy loss parameter)], obtained from computer modeling: (a) [4.19 eV, 0.41 eV]; and (b) [4.51 eV, 0.15 eV].

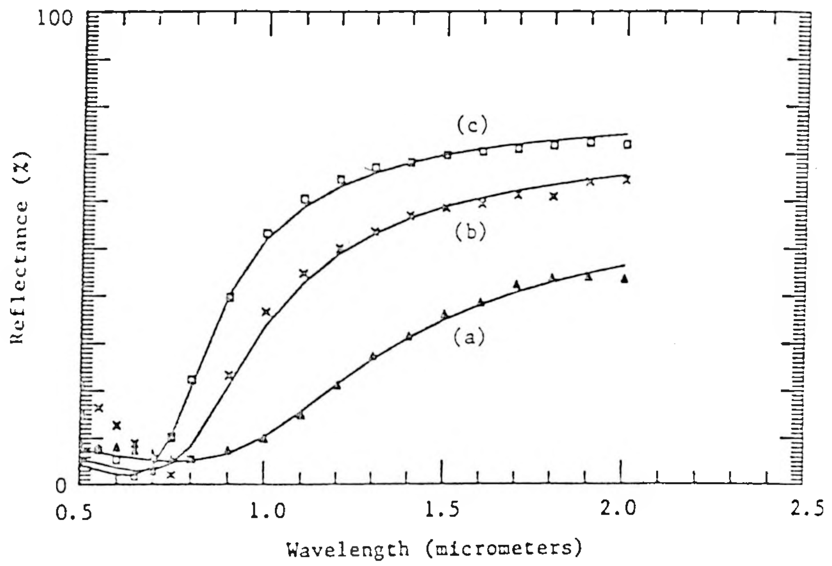

Figure 3. Reflectivity wavelength dependence for two Tufts-grown Li_xWO_3 crystals [(a) and (b)], and (c) a Li_xWO_3 crystal kindly supplied by S. Whittingham of SUNY-Binghamton [(c)]. [E_p,E_Γ] pairs = (a) [2.50 eV,0.76 eV]; (b) [3.05 eV, 0.55 eV]; and [3.29 eV, 0.42 eV].

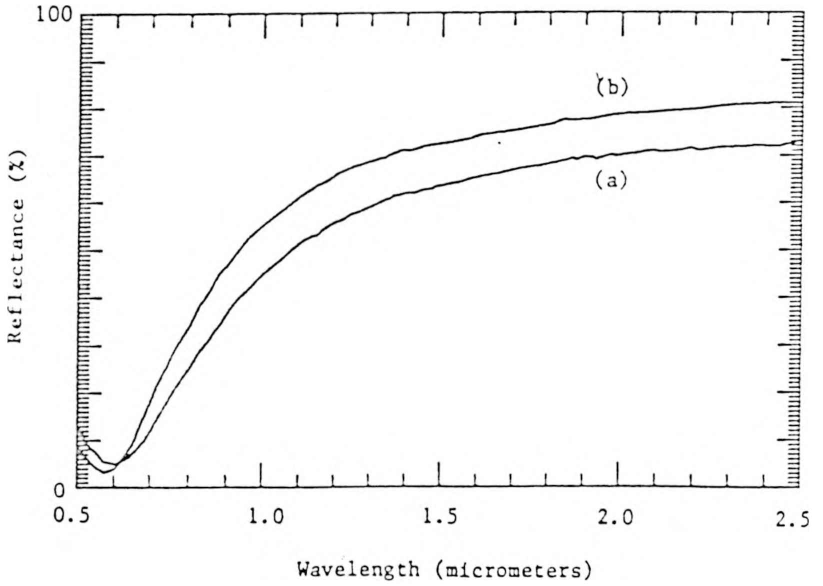

Figure 4. Reflectivity wavelength dependence for two polycrystalline Li_xWO_3 films. [E_p, E_Γ] = (a) [3.43 eV, 0.59 eV]; and (b) [3.50 eV, 0.42 eV].

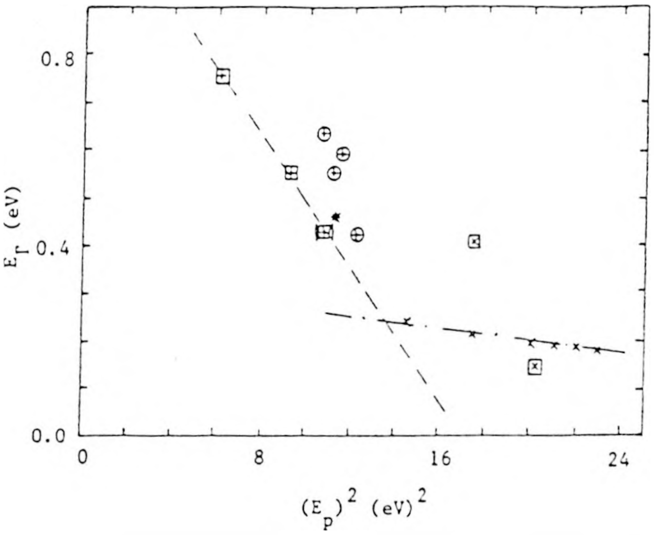

Figure 5. Drude energy loss parameter, E_Γ, versus square of the unscreened plasma energy, $(E_p)^2$, for bulk crystals of Na_xWO_3 and Li_xWO_3 and polycrystalline films of Li_xWO_3. ⊞ = crystals of Li_xWO_3; (⊞)* = Li_xWO_3 crystal provided by S. Whittingham; ⊕= polycrystalline film of Li_xWO_3; x = data from Ref.[3] for Na_xWO_3 crystal; and ⊠ = crystal of Na_xWO_3 (grown at Tufts University).

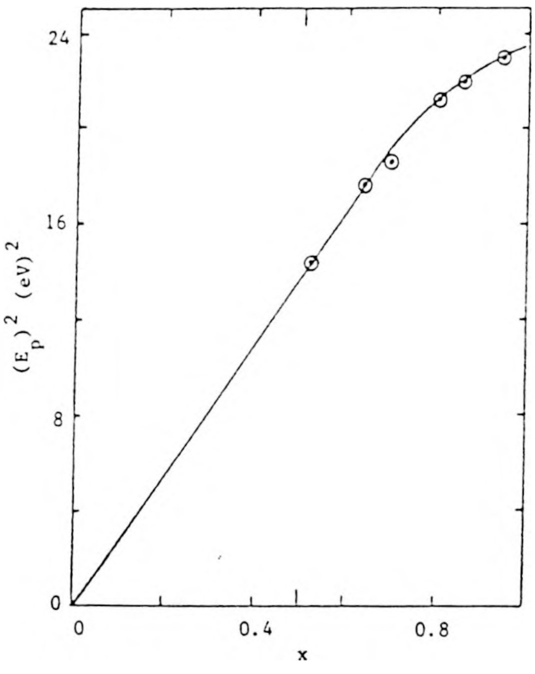

Figure 6. $(E_p)^2$ vs. x (effective molar ratio of lithium to tungsten), as derived from data of Owen et. al. [3]. (Please cf. current text for details.)

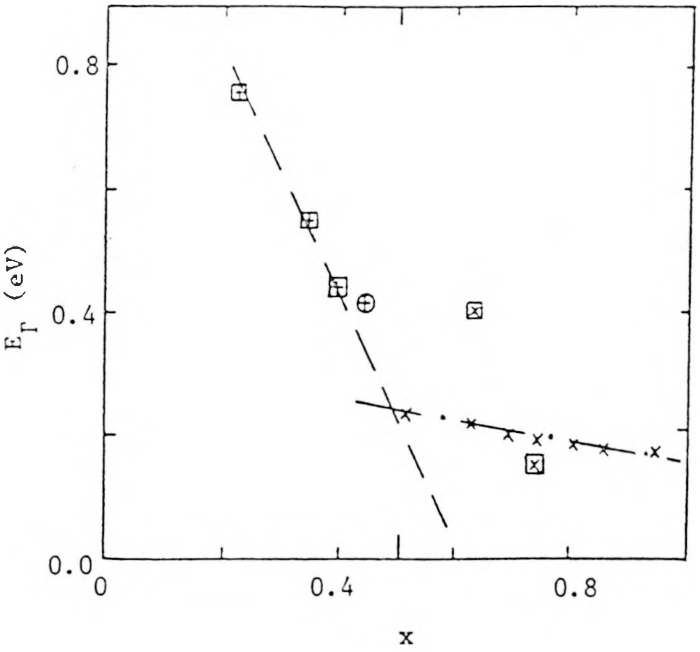

Figure 7. E_Γ vs. x using results of Figs. 5 and 6. Symbols are as defined in caption of Fig. 5.