

Raman resonant effects at the oxide interface in $W_xRe_{1-x}O_{3-y}$ mixed systems.

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Up to now, tungsten oxide (WO_3) has been the most used electrochromic material (1).

Appreciable blue coloration associated with electronically charged surface defects can be obtained, among others methods, by simple mechanical treatments like milling (2). In this case, the coloration effect is reversible after annealing treatments in oxidising atmosphere. Charged defects with specific optical absorption properties are induced also by the mixing of WO_3 with oxides having a different electronic configurations. In fact, the mixing of tungsten oxide with rhenium oxide, followed by high temperature treatment, induces coloration changes, from the pale yellow typical of bulk WO_3 toward a greyish-blue coloration.

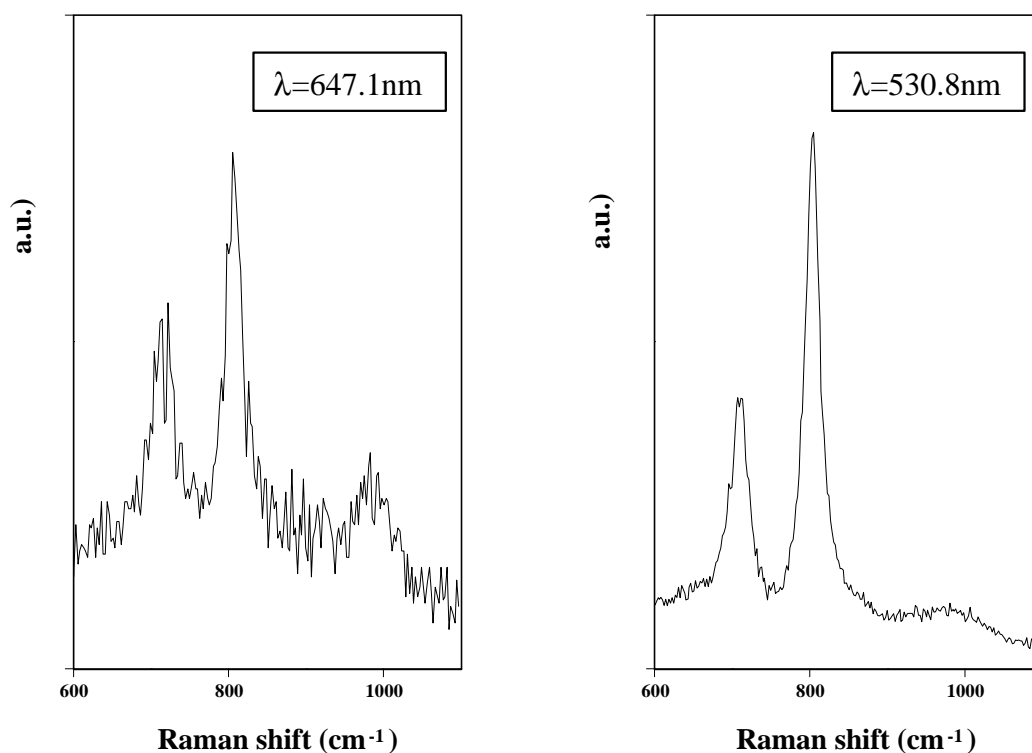
However, the bulk structure of WO_3 does not change. All the vibrational modes in the range $20-900\text{ cm}^{-1}$, for all the observable sample compositions, can be assigned to WO_3 dynamics. The Raman spectra of the mixed samples seem rather similar to the ones of monoclinic pure WO_3 . Results of Raman, XRD and EXAFS (2) suggest that particles of pure tungsten oxide, not too much perturbed in its crystal structure, are surrounded by zones of rhenium oxide.

Only a new, weak band at about 980 cm^{-1} appears in the spectra of the mixed samples. It can be compared with similar features at about 950 cm^{-1} , observed in pure WO_3 samples after milling. Similar bands of high intensity appears also in crystalline $WO_3 \cdot nH_2O$ (3) and amorphous WO_3 films and are usually assigned to a vibration of the $W=O$ double bond involving terminal oxygen.

A resonant effect for the 980 cm^{-1} band of the mixed samples is revealed by using different excitation laser sources. The relative intensity of the 980 cm^{-1} band, compared to the bulk stretching band at 800 cm^{-1} , appears noticeably higher for the red excitation light at 647.1 nm , with respect to the spectra excited by green or blue laser lines.

Such resonance effect is not observed in the similar band at 950 cm^{-1} of the pure ground WO_3 samples, thus suggesting a quite specific localization of the resonant vibration at the interface of tungsten oxide-rhenium oxide grains.

A model of the WO_3/ReO_2 interface is proposed, assuming the color centers are preferentially localized at the interfaces. The charge electroneutrality condition requires a reduction of the valence state from $6+$ to about $5.7+$ for interface tungsten ions, causing deep-blue coloration. The irreversibility of the color changes in mixed $\text{W}_x\text{Re}_{1-x}\text{O}_{3-y}$ against the oxidising action of the normal atmosphere allows to discard the hypothesis that the coloration is only due to free surface defects of grains, like in pure ground WO_3 .



1. C.G. Granqvist, Handbook on Inorganic Electrochromic Materials (Elsevier Science, Amsterdam, 1995).
2. E. Cazzanelli, C. Vinegoni, G. Mariotto, A. Kuzmin and J. Purans, Proc. 190th Electrochemical Society Meeting, Symposium on "Electrochromic materials and their applications III", San Antonio, TX, USA, October 1996,
3. M.F. Daniel, B. Desbat, J.C. Lessegues, B. Gerand, and M. Figlarz, J. Solid State Chem. **67**, 235 (1987).