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BRIEF COMMUNICATIONS

Evidence for Polaronic States in $Na_{0.1}WO_3$ from Raman Scattering

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Comparison of Raman spectra of WO_3 and $Na_{0.1}WO_3$ excited with 647- and 488-nm radiation shows preresonance Raman enhancement of overtone intensity in a W–O stretching mode for $Na_{0.1}WO_3$ under 647-nm excitation. This observation supports the idea that electrons are trapped in polaronic states in the low x sodium tungsten bronzes. © 1989 Academic Press, Inc.

1. Introduction

Tungsten trioxide is a pale yellow d^0 oxide, but it assumes a characteristic blue or grey coloration when doped with small concentrations of sodium, hydrogen, or other donor atoms. The coloration is associated with a new electronic excitation centered at about 1.4 eV. The nature of the excitation responsible for the color band is of particular interest in view of the application of WO_3 films in electrochromic display devices. On the basis of transport and other measurements (*1–4*) it is widely believed that at low sodium doping levels ($x < 0.26$ in Na_xWO_3) the sodium tungsten bronzes are nonmetallic with localized W^{5+} and W^{6+} ions. Related data for reduced tungsten oxide WO_{3-x} also point to the existence of localized polaronic and bipolaronic states (*5, 6*). In this model the blue coloration is associated with intervalence charge transfer excitation from localized W^{5+} polaronic states to adjacent W^{6+} sites (*7, 8*). Alternatively Hollinger and co-workers (*9*) suggest charge transfer from the O:2*p* valence band to "split-off" W^{5+} states. However it has been argued on the basis of new transport and optical data for thin film material that the low x tungsten bronzes are essentially metallic (*10, 11*) and that the blue color is due to interband excitation from occupied W:5*d* conduction band states into higher tungsten states and states derived from sodium 3*s* orbitals. In the present communication we apply Raman spectroscopy to the study of the low sodium tungsten bronze $Na_{0.1}WO_3$. There is evidence of a preresonance Raman enhancement of overtone intensity in a W–O stretching mode when spectra are excited with the red line of a krypton laser at 647 nm ($h\nu = 1.92$ eV) whose frequency falls on the wing of the color band. This observation supports the view that the color band electronic excitation is strongly coupled to

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W–O stretching modes of the lattice and thus that the coloration is indeed due to polaronic charge transfer excitation.

2. Experimental

$Na_{0.1}WO_3$ and other tungsten bronzes studied for purposes of comparison were prepared by reaction between Na_2WO_4, WO_3, and W metal is sealed, evacuated quartz tubes at 800°C. Characterization of the samples prepared in this way has been discussed previously (*12*). Note in particular that the sample of $Na_{0.1}WO_3$ gave a tetragonal powder diffraction pattern characteristic of the so-called tetragonal I phase. Samples were pressed into 13-mm diameter pellets between tungsten carbide dies and mounted in a spinning attachment for study by Raman spectroscopy. Spectra were excited by the 488-nm ($h\nu = 2.54$ eV) line of an Ar^+ laser and the 647-nm ($h\nu = 1.92$ eV) line of a Kr^+ laser (Coherent). The $Na_{0.1}WO_3$ sample proved to be particularly sensitive to damage by the red krypton line and both rapid sample spinning and moderate laser powers (<150 W) were necessary for measurement of satisfactory spectra. Scattered radiation was dispersed with a Spex Ramalog 5 double monochromator and photon counted with a thermoelectrically cooled detector.

3. Results and Discussion

Discussion of the Raman spectra necessitates consideration of the symmetry properties of the tungsten bronzes. All are based on corner-sharing WO_6 octahedra. In the idealized cubic form of WO_3 there is one formula unit per cell and the optical modes span irreducible representations Γ as follows:

$$\Gamma = 2T_{1u} + T_{2u}.$$

One of the T_{1u} modes near 800 cm^{-1} can be classified as an asymmetric O–W–O stretch, while the other T_{1u} mode near 300 cm^{-1} has dominant O–W–O bending character. For cubic tungsten bronzes ($x > 0.4$) there is an additional T_{1u} low-frequency mode associated with rattling of Na^+ ions relative to the framework octahedra (*13*). Note that none of these modes is Raman active. The monoclinic structure adopted by WO_3 around room temperature contains eight formula units per cell and the 93 W–O optical lattice modes now span irreducible representations as follows (*14*):

$$\Gamma = 24(A_g + B_g) + 23A_u + 22B_u.$$

The 48 grade modes are all Raman active. It is unnecessary for present purposes to attempt a detailed group theoretical classification of the overlapping band systems; rather we can classify modes around 800 cm^{-1} in a loose way as W–O stretching modes. Finally, the tetragonal structure of $Na_{0.1}WO_3$ has two WO_3 units per cell so that we now have 21 W–O optical lattice modes. It is again useful to designate modes around 800 cm^{-1} as W–O stretching modes.

Turning now to the experimental spectra of WO_3, $Na_{0.1}WO_3$, and $Na_{0.65}WO_3$ shown in Fig. 1, we find in all three spectra two bands around 800 cm^{-1} in the W–O stretching region. The spectrum of WO_3 itself agrees with previously published data (*14*). The observation of Raman active modes for $Na_{0.65}WO_3$ is surprising given the nominally cubic structure of this material. However, careful neutron scattering studies (*15*) of cubic tungsten bronzes reveal small deviations from perfect cubic symmetry and the observation of the Raman modes is presumably a consequence of this distortion. However, the Raman modes are very weak for the cubic metallic material.

The spectra from the polycrystalline tungsten bronzes all displayed a strong background due to fluorescence from surface hydroxyl groups. This background was particularly problematic for $Na_{0.1}WO_3$. Under 488-nm excitation, overtone structure

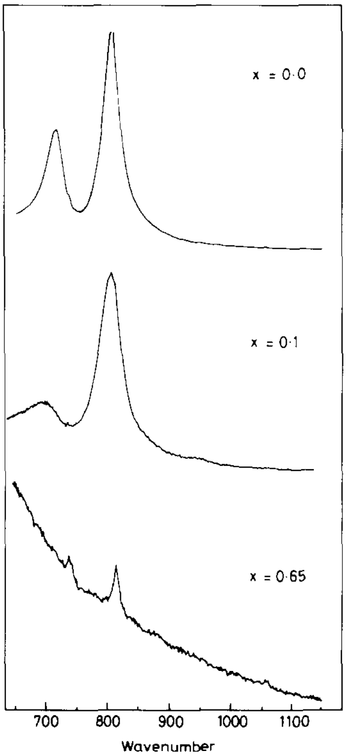

FIG. 1. Raman spectra of Na_xWO_3 in W–O stretching region excited with a 488-nm line of argon ion laser.

could barely be discerned above the fluorescent background for $Na_{0.1}WO_3$ although we can be reasonably confident that the overtone intensity is no stronger than for WO_3 itself where the background is somewhat weaker (Fig. 2). The frequencies of the overtones for WO_3 are just below twice those of the fundamentals, indicating only small anharmonicity. Under 647-nm excitation, overtone structure for WO_3 is even weaker than with the 488-nm blue line. However for $Na_{0.1}WO_3$ we observed overtone structure about a factor of 100 stronger than for WO_3 under the red line excitation and at least a factor of 10 stronger than for $Na_{0.1}WO_3$ itself under blue line excitation (Fig. 3). A further observation is that the overtone band now appears to consist of two overlapping components, one centered at about 1600 cm^{-1} as in WO_3, but with a new component at 1530 cm^{-1}.

Consider now the polaron model for $Na_{0.1}WO_3$. Electrons introduced by sodium doping are trapped at W sites by local polarization of the dielectric lattice around the trap site. In microscopic terms electron trapping converts regular W^{6+} ions into W^{5+} and the polarization corresponds to elongation of W–O bonds at the W^{5+} sites. The electron is trapped by distortion of W–O bonds along the normal coordinate of a totally symmetric breathing mode of a WO_6

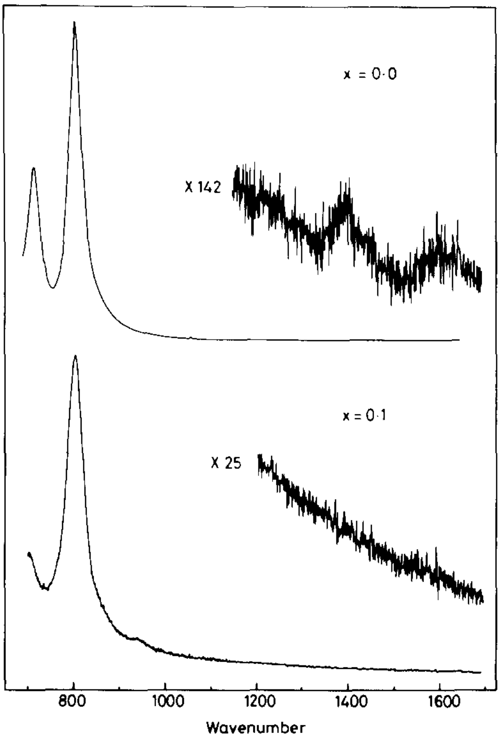

FIG. 2. Raman spectra of WO_3 and $Na_{0.1}WO_3$ excited with a 488-nm line of argon ion laser, showing overtones for WO_3. The ratio between the peak intensity of the overtone for WO_3 at 1602 cm^{-1} and the fundamental at 807 cm^{-1} is about 6×10^{-4}. For $Na_{0.1}WO_3$ the overtone of the 803 cm^{-1} band at around 1600 cm^{-1} is not discernible above the strong fluorescent background, but the intensity ratio cannot be much greater than for WO_3.

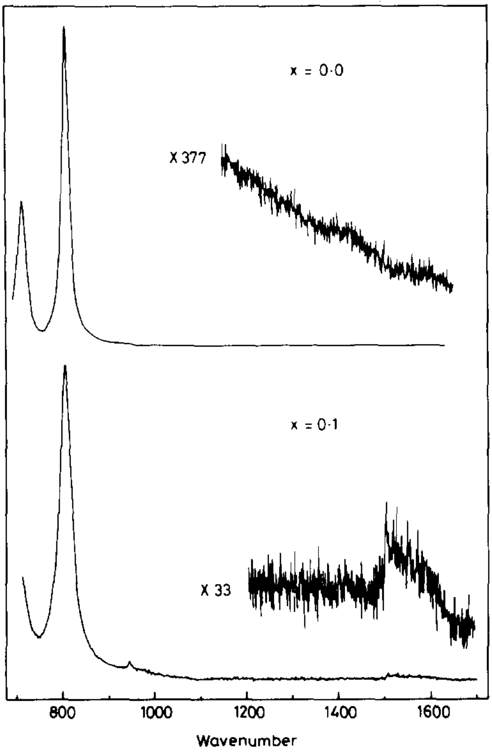

FIG. 3. Raman spectra of WO_3 and $Na_{0.1}WO_3$ excited with a 647-nm line of krypton ion laser. For WO_3 the intensity ratio between the 1602 cm^{-1} overtone and the 807 cm^{-1} fundamental is now only about 5×10^{-5}, but for $Na_{0.1}WO_3$ the overtone peak height is now 6×10^{-3} that of the fundamental. Note also that the overtone maximizes at 1530 cm^{-1}, well below twice the frequency of the fundamental. There is also a shoulder at about 1600 cm^{-1}.

octahedron. Note that the frequency of the local mode trapping the electron is expected to be somewhat below that of the original W–O lattice modes which relate to W^{6+}–O stretches rather than W^{5+}–O stretches. The absorption maximizing at 1.4 eV arises from an excitation in which an electron is promoted vertically from the potential curve trapping the electron at the W^{5+} site to the potential curve trapping the electron on an adjacent site. In a Raman experiment it is well established that resonance enhancement of fundamental and especially overtone intensity is observed when the exciting radiation corresponds in frequency with an electronic absorbtion band strongly coupled to the vibrational mode of interest (*16*). Thus in the mixed-valence compound Cs_2SbCl_6 excitation of Raman spectra at frequencies corresponding to that of the intervalence charge transfer band leads to overtone progressions in the a_{1g} breathing mode of the $SbCl_6^-$ octahedron (*17*). In the present case the red laser line at 1.92 eV is seen to lie sufficiently close to the maximum of the polaronic absorption band to lead to modest resonance enhancement of the overtone intensity both in the local vibrational mode trapping the electron and in the stretching mode of the WO_6 octahedron to which charge transfer takes place. The fundamental of the resonance enhanced local W^{5+}–O mode is not resolved in our experiments but this is not surprising because it must lie around 765 cm^{-1} where it overlaps the broadband centered at 800 cm^{-1} due to the nonenhanced parent W–O lattice modes. However, the overtone intensity for the nonresonance enhanced W–O stretches is negligible, so that in the overtone region we are able to observe the expected downward shift in frequency associated with the trapped electrons.

An obvious extension of the present work is to use a near infrared excitation source for the Raman experiments even more closely matched to the position of the polaronic absorption band. We are also engaged in further systematic study of Raman spectra of both cubic and noncubic tungsten bronzes.

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