

# Electronic Structure Studies of $\text{Na}_x\text{WO}_3$ Using X-ray Absorption Near-Edge Spectroscopy

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## X선 흡수분광법을 이용한 $\text{Na}_x\text{WO}_3$ 전자구조 연구

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### Abstract

X-ray absorption near-edge spectroscopy (XANES) investigations have been carried out over the concentration range  $0.5 < x < 1$  of the sodium tungsten bronze system  $\text{Na}_x\text{WO}_3$ . Spectral features which vary systematically with the amount of sodium ( $x$ ) are identified for the nonstoichiometric compounds. Na content variation induces a variation in the white line (WL) intensity in these  $\text{Na}_x\text{WO}_3$  materials. The WL decreases upon Na addition is quantitatively consistent with the one Na electron donated to the W 5d-band. This result is consistent with the theoretical calculations of the band structure of these materials, and the filling of the conduction band with increasing  $x$  is explicitly demonstrated. Moreover, this XANES method provides a much more direct proof of charge donation to the W d-band. The small but discernible shift in the continuum resonance reflects due to the Na induced lattice expansion.

### 요 약

$x$ 의 범위가  $0.5 < x < 1$ 인 sodium tungsten bronze( $\text{Na}_x\text{WO}_3$ )에 대한 흡수끝 광흡수 분광 연구가 수행되었다.  $\text{Na}(x)$ 의 농도에 따라 분광스펙트럼이 체계적으로 변화됨이 밝혀졌다.  $\text{Na}(x)$ 의 변화에 따라  $\text{Na}_x\text{WO}_3$  물질의 white line(WL) 크기가 변화함을 알았다. Na 첨가에 따른 WL 크기의 감소는 W 5d 밴드에 한 개의 Na 전자가 증여된다는 사실과 일치한다. 이 결과는 이론적인 밴드구조 계산 결과와 일치하며,  $x$ 가 증가함에 따라 전도대가 채워진다는 것을 명백하게 보였다. 흡수끝 광흡수 분광법은 W의 d 밴드로의 전하증여에 대한 직접적인 증거를 제공하였다. 작지만 명백한 continuum resonance의 이동은 Na 첨가에 따른 격자상수 팽창에 의한 것으로 밝혀졌다.

### 1. Introduction

The tungsten bronzes form a group of largely non-stoichiometric compounds of general formula  $\text{M}_x\text{WO}_3$ , where M is an electropositive elements, typically an alkali metal. These materials are: a Mott-type insulator for  $x < 0.24$ <sup>1)</sup>; a superconductor with a tetragonal structure of  $0.24 < x < 0.49$ <sup>2)</sup>; and a metallic simple-cubic perovskite for  $0.5 < x < 1$ .<sup>3)</sup> The crystal structure has high symmetry for high  $x$  val-

ues and low symmetry for low  $x$  values. Here we are concerned with the properties of  $\text{Na}_x\text{WO}_3$  in this last range where the structure is cubic. The cubic perovskite structure is illustrated in Fig. 1. In the unit cell tungsten atoms are at the cube centers (solid circle), oxygen atoms are at the face centers (open circle), and sodium atoms are distributed at the cube corners (shaded circle, when  $x=1$ , all the corners will be occupied by sodium atoms).

Since Matthias and coworkers<sup>2)</sup> first discovered

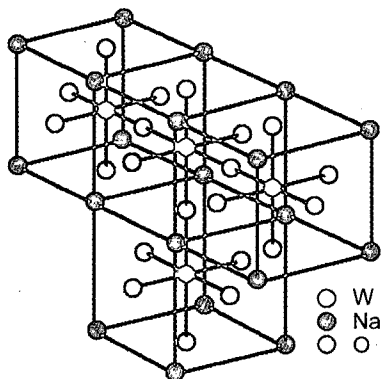


Fig 1.  $\text{ABO}_3$  cubic perovskite structure. The open circles represent oxygen ions, the solid circles indicate the transition-metal B ions (W ions), and the shaded circles represent the A ions (Na ions).

superconductivity in the tungsten bronzes, there has been a continuing interest in these materials because so many of their properties can be continuously altered by adding atoms into the open channels of the basic  $\text{WO}_3$  structures. For example, as sodium is added to  $\text{WO}_3$  it contributes conduction electrons to the energy bands and the electronic properties change markedly. Indeed, a number of different crystal structure form, some of which are semiconducting and some metallic, depending on the Na concentration. The band structure is highly anisotropic and the cubic bronzes have a nested character, so these compounds may be reasonable candidates for materials which show electronically driven phase changes such as charge density waves.<sup>4)</sup> The composition of the present study is limited to the cubic phase of these materials, which is stable in the range  $0.5 < x < 1$ . In this range the materials exhibit the metallic properties of luster and high electrical and thermal conductivities. One of the purposes of this work is to survey the behavior of the W d-band and its correlation with the Na concentration by using x-ray absorption near-edge spectroscopy (XANES).

## 2. Experimental

The sodium tungsten bronze samples used in this investigation were single crystals prepared by the electrolytic reduction of a fused mixture of sodium tungstate and tungsten trioxide, which was prepared

by dehydration of tungstic acid.<sup>5)</sup> Precision lattice constants of our samples were obtained by the x-ray powder diffraction method using  $\text{Cu K}_{\alpha 1}$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ) and an automated SCINTAG-PAD-V powder diffractometer. A high purity silicon powder was used as an internal standard. There is a variation in the lattice constant of the crystals corresponding to variation with increasing values  $x$ . All our samples had been characterized by x-ray lattice constant measurement. The lattice constant ( $a_0$ ) is known to give a measure of  $x$  through use of the relationship  $a_0 = 0.0820x + 3.7845 \text{ \AA}$ .<sup>3)</sup> All of the bronzes were in the range of cubic symmetry.

X-ray absorption measurements were carried out on line X19A of the 2.5 GeV National Synchrotron Light Source (NSLS) synchrotron radiation at Brookhaven National Laboratory. X-ray energy was varied using a Si(111) double-crystal monochromator that was detuned by  $\sim 30\%$  to minimize high order harmonics in the x-ray beam. W  $L_3$ -edge spectra of  $\text{Na}_x\text{WO}_3$  samples were recorded in transmission mode. For transmission XANES measurement the samples were ground and brushed onto Scotch tape. About two layers of tape constituted the sample so that thickness effects and particle size effects should be negligible.

## 3. Results and discussion

The bronzes used in the present studies are listed in Table 1. On the basis of x-ray diffraction data, the bronzes are cubic, and  $a_0$  values were 3.829, 3.837, and 3.849  $\text{\AA}$ . Figure 2 shows the W  $L_3$  absorption near-edge spectra obtained for sodium tungsten bronzes. These spectra were background subtracted by fitting the pre-edge background. The spectra were then normalized with the multiplication by a factor which makes the continuum step

Table 1. Showing lattice parameter ( $a_0$ ), sodium composition ( $x$ ), and color of the samples

Sample	$a_0$ ( $\text{\AA}$ )	$x$	Color
A	3.829	0.57	red
B	3.837	0.65	orange
C	3.849	0.79	golden yellow

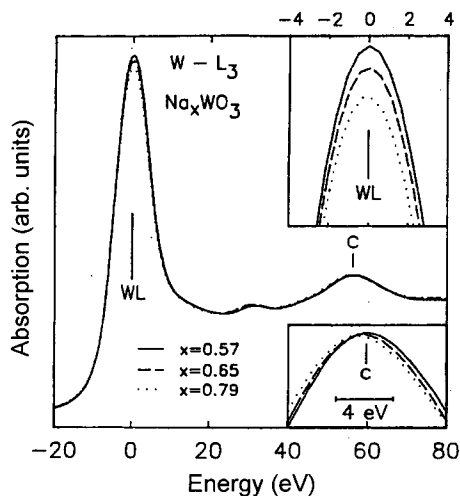


Fig. 2. W  $L_3$  spectra for  $\text{Na}_x\text{WO}_3$  compounds illustrating the WL area decrease due to W 5d-orbital filling and c-feature shift to lower energy due to the W-O bond length dilation with increasing  $x$ .

equal to unity at the higher energy region. Absorption at the  $L_3$ -edge corresponds to the excitation of a  $2p_{3/2}$  electron to unoccupied states above the Fermi level. Dipole selection rules dictate that the final state must be of s or d symmetry. However, and calculations have shown that transitions at the  $L_3$ -edge are dominated by final states of d symmetry.<sup>6)</sup> The 5d band of the third row transition elements is progressively filled as one moves to the right along the periodic table. The intense white line (WL) observed in the  $L_3$  edge of transition metals is related with a higher density of unoccupied d states at the Fermi level.<sup>7)</sup> Na content variation may induce a variation in the WL intensity in these  $\text{Na}_x\text{WO}_3$  materials, indicating that the W 5d electron states increase upon adding the sodium atom.

The electronic structure of the metallic cubic  $\text{Na}_x\text{WO}_3$  bronzes has been extensively studied.<sup>8-10)</sup> The band structure can be readily understood in terms of tight-binding wave functions formed by combinations of the oxygen 2p and W 5d orbitals.<sup>11)</sup> The metal  $e_g$  5d states admix only with one of the three p states of each oxygen atom giving rise to two pairs of  $\sigma$  bands and an oxygen flat band. On the other hand, each of the three  $t_{2g}$  5d states admix only with two oxygen p states giving rise to three oxygen flat bands and three pairs of  $\pi$  bands. For

the hypothetical cubic  $\text{WO}_3$ , the 6 d-electrons from tungsten and the  $3 \times 4$  electrons from the three oxygen fill these bands up to the energy gap which lies between the O 2p and W 5d atomic levels. For  $\text{Na}_x\text{WO}_3$ , the fractional extra electron from the Na appears in the  $\pi$ -antibonding conduction band. Using Hall-effect measurements Lightsey *et al.*<sup>12)</sup> showed that the number of conduction electrons increases with  $x$  for  $x > 0.22$ , the absolute number of electrons being very nearly equal to one per sodium atom. The WL decrease upon Na addition in these  $\text{Na}_x\text{WO}_3$  materials is quantitatively consistent with the one Na electron being donated to the W 5d-band as proposed in the past. This gives evidence for the filling of the conduction band as  $x$  increases. This constitutes a further support for the homogeneous nature of the bronzes, and appears to be consistent with a model in which electrons freed from Na atoms fill a rigid band.<sup>13)</sup> Moreover this XANES method provides a much more direct proof of charge donation to the W d-band.

Spectral features after WL feature in XANES regime are typically caused by multiple elastic back-scattering paths of the photoelectrons and by virtual bound molecular orbitals. These two viewpoints are essentially equivalent and both mandate that the XANES spectra contain information on the near neighbor interatomic distances.<sup>14-16)</sup> A particularly strong feature, in this region, is typical in compounds where a metallic atom (M) is surrounded by a shell of strongly electronegative ligands, and is referred as a continuum resonance (CR) features. The feature c in Fig. 2 is interpreted as a continuum resonances due to the O ligand shell about W.

A continuum resonance in an x-ray absorption near-edge spectrum can occur when there exists a pronounced local maximum in potential surrounding the atom being excited. In such a case vestiges of a bound-localized state of this potential can exist just above the escape threshold for photoelectrons. The potential due to this ligand shell can cause a resonance in the continuum outgoing photoelectron spectrum for electronic  $k$  values (wavelength) close to the ligand-shell geometrical resonance. The resonance energy is going to be inversely proportional to the square of ligand shell distance. The small but

discernible shift in the c-feature between the  $x=0.57$  and  $x=0.79$  spectra is illustrated in the inset of Fig. 2. The energy shift of this c feature reflects due to the Na induced lattice expansion. The energy of this CR feature falls in good agreement with our other transition metal oxide compounds. Thus in a sense this shift is a different confirmation of this features to variations in the W-O bond length. Several authors have put forward theories based on multiple scattering or band structure calculations to describe the strong c-feature in this region.<sup>17-19)</sup> In most cases the theory has been used to explain transitions in a specific model compound, but to date there has been little or no efforts to generalize these ideas to related class of compounds with varying ligand shell size.

#### 4. Conclusions

We have presented structural results from x-ray diffraction and  $L_3$  edge XANES on sodium tungsten bronzes. The density of unoccupied W 5d states in the  $\text{Na}_x\text{WO}_3$  are modified due to the charge donation from Na, and this is supported by the WL area decrease at W  $L_3$  edge. The empty density of W 5d states is reduced monotonously with increasing Na concentration. The variation of the amount of charge transfer to W 5d band is consistent with the theoretical calculations of the band structure of these materials.

An analysis of the continuum resonance feature appearing in  $L_3$  near-edge spectra of sodium tungsten bronzes indicates an empirical relationship between interatomic distances and resonance energy (referenced to the white line peak position). As expected from simple quantum box analogy and/or multiple scattering theory, we find that the relative position of continuum resonance is inversely proportional to the square of near neighbor interatomic distance.

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