Investigations of the Anisotropic Optical Reflectivity of Binary and Ternary Nb–W Oxides Possessing Block-Type Crystal Structure *

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We have studied the anisotropic optical properties of binary $NbO_{2.5-\delta}$ $(0 < \delta \leq 0.083)$ and ternary $Nb_{18-\varepsilon}W_{8+\varepsilon}O_{69}$ $(\varepsilon = 0, 1, \ldots, 9)$ compounds using the polarized regular-reflection method. We observed strong anisotropic behaviour for all reduced phases. The anisotropic effect can be related to the crystallographical structure principle and to the doping of charge carriers by the reduction of oxygen (δ) or substitution of W for Nb (ε) in the binary and ternary oxides, respectively. Our results indicate that the charge carriers are confined to the structural block units. For increasing δ and ε, metal-like properties occur ($\delta \geq 0.1$, $\varepsilon > 8$) in the infinite block direction only.

Key words: Optical reflectivity; Block-type crystal structure; Niobium oxide; Niobium tungsten oxide.

1. Introduction

Niobium and niobium-tungsten oxides are known to possess so-called “Block-Type Structures” [1]. Gatehouse and Wadsley [2] have shown that the structural building principle of this type of compounds consists of columns of $n \times m \times \infty$ $[MeO_6]$ octahedra (Me = Nb or W) that are only top-shared. Typical values of n and m are 3, 4 and 5. The block columns are linked together by edge-shared octahedra yielding two sets of “shear planes”, which are perpendicular to each other. Therefore, ordinary “ReO_3”-type structure is observed only within the blocks. This structural building principle has been verified by many groups of authors, especially in the field of high-resolution transmission electron (HRTEM) studies (e.g. [3–5]).

For the binary $NbO_{2.5-\delta}$ block-type family different phases with definite degree of reduction (δ) are known in the range of compositions $0 \leq \delta \leq 0.083$, e.g. $NbO_{2.417}$ $(\equiv Nb_{12}O_{29})$, $NbO_{2.454}$ $(\equiv Nb_{22}O_{54})$, $NbO_{2.491}$ $(\equiv Nb_{53}O_{132})$, $NbO_{2.5}$ $(\equiv Nb_{28}O_{70})$ (see [6]). The ternary system reveals series of solid solution of definite metal to oxygen atomic ratios: e.g. Me/O = 26/69 for $Nb_{18-\varepsilon}W_{8+\varepsilon}O_{69}$ (see [7]). In first investigations of their electrical conductivity and optical absorption it was shown that electrons are doped: (i) in the case of binary $NbO_{2.5-\delta}$ by oxygen reduction [8] and (ii) in the case of ternary compounds by the substitution of Nb with W [9]. The fully oxidized end-members of the series (i.e. $\delta = 0$, $\varepsilon = 0$) show an optical bandgap of about 3 eV between a lower (filled) oxygen 2p valence and a higher (empty) “Me” d conduction band. When increasing the degree of reduction (δ, ε) an absorption band with its maximum in the energy range 0.5–0.8 eV develops, indicating the appearance of new electronic states within the gap. It has been shown in earlier studies [8, 9] that the analysis of the line profiles of the absorption band together with the semiconducting properties (thermal activation energies $E_a \leq 0.2$ eV) strongly support the small-polaron nature of these states. Both the binary and ternary system undergo Anderson-type metal–insulator transition, i.e. for increasing δ and ε, respectively, phases with metallic properties occur. Critical carrier concentrations for this transition are about $2 \cdot 10^{21}$ cm^{-3} and $6 \cdot 10^{21}$ cm^{-3} for the binary and ternary system, respectively.

In this study we report for the first time on the anisotropic properties observed in the visible and near-infrared spectral range. We shall discuss our results with respect to the structural building scheme.

2. Experimental

Single crystals have been prepared by chemical transport reactions. Details of the preparation procedure and characterization are described by Hussain et

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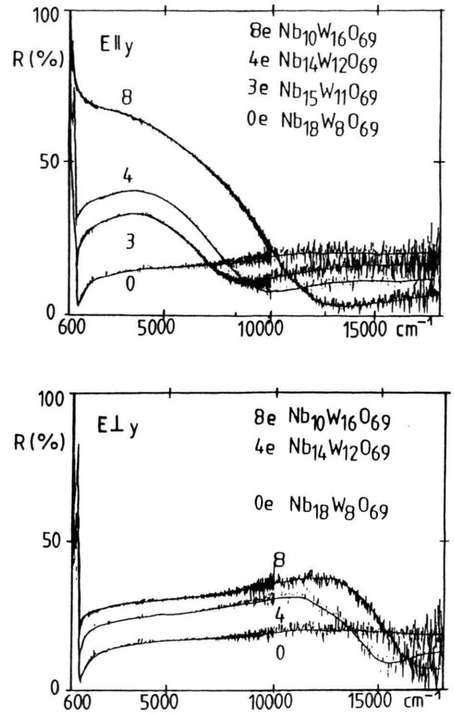

Fig. 1. Reflectivity of $Nb_{18-\varepsilon}W_{8+\varepsilon}O_{69}$ observed for $E \parallel y$ (1 a) and $E \perp y$ (1 b), respectively. Only spectra of some selected compositions are shown for clarity (see text). The number of "free electrons", expected from the chemical formula with the assumption of Nb^{5+}, W^{6+} and O^{2-} oxidation states, is given in the Figure (this number is equal to ε).

al. [6] and Groh et al. [7] for the binary and ternary system, respectively. Small crystals were separated from the products of the various compositions, which have been the same as used in the earlier studies [8, 9]. All crystals investigated in this study are needle-shaped (typically $1 \times 0.5 \times 0.5$ mm^3). The growth axis of the crystals is always parallel to the y-axis of the crystal lattice and coincides with the direction of infinite extension of the blocks. The crystals were glued to the sample holder with such an orientation that we could measure the reflectivity of planes with the y-axis within and perpendicular to the crystal surfaces. The crystal surfaces were polished for the measurements ($\frac{1}{4}$ μm diamond paste in the final step). The reflection data were taken at nearly normal incidence of the polarized light using an FTIR spectrometer (Bruker IFS 88) with an attached microscope. The spot size was chosen to be 50 μm and well inside of some microfractures and twins of the crystals, as observed in the microscope.

3. Results

We have done measurements on a whole series of solid solutions of $Nb_{18-\varepsilon}W_{8+\varepsilon}O_{69}$ with compositions $\varepsilon = 0, 1, \ldots, 9$. Typical spectra of the ternary system for the electrical field polarized parallel and perpendicular to the y-axis are shown in Figs. 1 a and 1 b, respectively. For the sake of clarity we have shown only a selection of spectra, which, however, represent the general behaviour. The undoped samples (see spectra for $Nb_{18}W_8O_{69}$) show typical insulator spectra with phonon lines for wavenumbers $\lesssim 1000$ cm^{-1}. With increasing W content the reflectivity becomes dramatically anisotropic:

i) For $E \perp y$ a resonance-like feature increases that can typically be described by a Lorentz oscillator of eigenfrequency of about 10 000 cm^{-1}.

ii) Similar to the 10 000 cm^{-1} feature in the $E \perp y$ spectra, but by far more intense, a feature centred at about 5000 cm^{-1} evolves with increasing doping in the $E \parallel y$ spectra.

It should be noted that the "oscillator-like" feature changes to a "plasma-like" feature for the highest doping concentrations. This change coincides with the metal–insulator transition observed in the electrical conduction behaviour, which was measured for the electrical field along the y-axis [9].

Qualitatively similar behaviour is observed for the binary $NbO_{2.5-\delta}$ phases (see Figs. 2 a, b). We note that the $NbO_{2.5-\delta}$ composition with $\delta = 0.005$ belongs crystallographically to the $NbO_{2.5}$ phase, i.e. it is not an ideal composition of a separated phase. However, it deviates completely from the parent phase $NbO_{2.5}$, showing high electronic conductivity with an Arrhenius activation energy of $E_a \approx 0.05$ eV [8]. For comparison, the intrinsic activation energy of $NbO_{2.5}$ is $E_a \approx 1.5$ eV [8]. Therefore, comparing the $E \parallel y$ and the $E \perp y$ spectra of the $NbO_{2.495}$ sample, we argue that the difference in the observed spectra is entirely related to the states introduced by the reduction, i.e. by the charge carriers (polarons). The $E \perp y$ spectra of $NbO_{2.495}$ can furthermore not be distinguished from the $E \perp y$ and $E \parallel y$ ones of the non-reduced phase $NbO_{2.5}$ within our resolution. From these results we conclude that a strong anisotropic behaviour is already present for a small degree of reduction ($\delta < 0.01$). For $NbO_{2.5-\delta}$ samples with $\delta \geq 0.01$ the $E \parallel y$ spectra reveal plasma-like features, indicating metallic properties for these phases along the y-axis. Measurements of the conductivity with the electrical field along the y-axis have

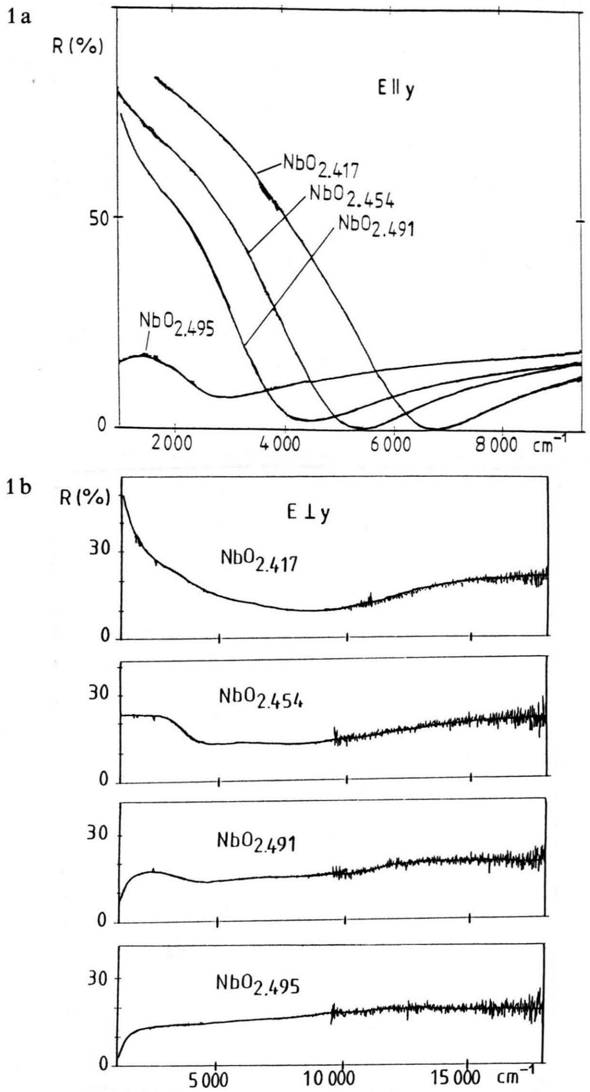

Fig. 2. Reflectivity of $NbO_{2.5-x}$ compositions (as given) observed for $E \parallel y$ (2a) and $E \perp y$ (2b).

shown metallic conduction behaviour for phases with $\delta > 0.01$ [8].

4. Discussion

Without going into details of the line profile features (details will be given elsewhere [10]), the general features of the spectra can be correlated with the structural scheme and the appearance of charge carriers. For a better understanding of the main idea we have

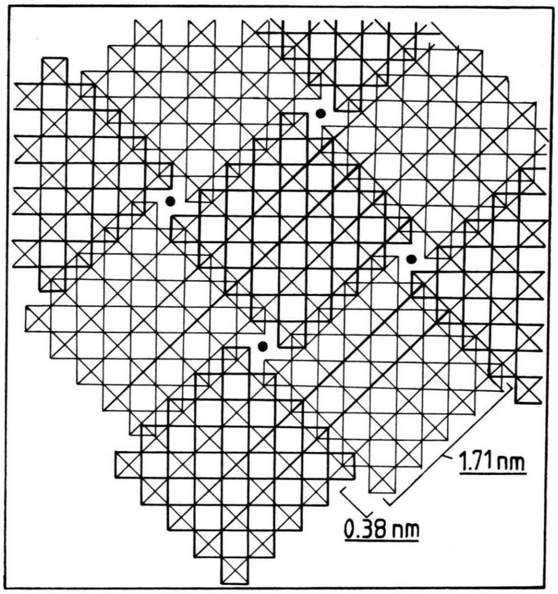

Fig. 3a. Structural scheme of the 5 × 5 block-type structure in projection along the crystallographic y-axis. The lattice parameter b is given by $b \approx 0.38$ nm, i.e. one octahedral diameter (a scale is given also for one block diameter). Note that inside the blocks only top-shared octahedra exist. The blocks are linked together by edge sharing of the octahedra. Therefore the $x-z$ planes of neighbouring blocks are shifted by $z = b/2$. The black spots indicate the position of tetrahedrally coordinated Me-sites, which are located at $z = b/4$ and $3b/4$ (for the 26th Me-atom as given by the chemical formula). In the projection "shear planes" can be distinguished from the blocks by the smaller and larger empty squares, respectively.

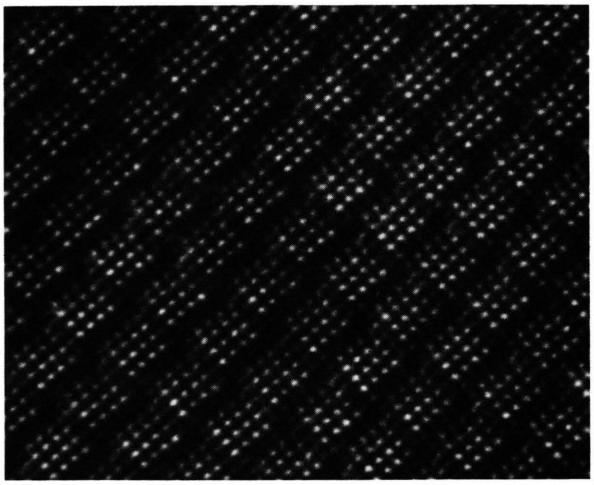

Fig. 3b. Typical HRTEM photograph of a 5 × 5 block-type compound ($Nb_{16}W_{10}O_{69}$). The structural principle can be well observed in relation to the model: regions of shear planes (darker strings with the appearance of small light spots; see smaller empty squares in the structural scheme) and top-shared octahedra (darker centre with lighter spots).

depicted in Fig. 3a a projection of the structural building scheme (along the *y*-axis) typical for the $Nb_{18-\varepsilon}W_{8+\varepsilon}O_{69}$ series of compounds. In Fig. 3b a HRTEM photograph of a sample with chemical composition $\varepsilon = 2$ is shown that has been observed for the electron beam parallel to the *y*-axis. The model in Fig. 3a idealizes the appearance of top-shared MeO_6 octahedra within the 5 × 5 blocks by filled and empty squares. Smaller empty squares are observed along the block intersections, resulting from the corner sharing of octahedra. The main structural features can also be observed from the HRTEM photograph. The reflection measurements were done with respect to the *y*-axis of cuts that are not shown in Fig. 3. However, we have also checked the anisotropic reflectivity of the (010)-plane, which is in these systems always parallel to the $x-z$ plane, i.e. the plane of projection in Figure 3. The resulting spectra reproduce fairly well the features of the appropriate $E \perp y$ spectra. Accordingly, the observed properties show that the strong increase of the near-infrared reflectivity points towards the block axis, i.e. in the *y*-direction. This implies also that metallization at high doping concentrations could occur only in the block direction with infinite extension. Therefore we suggest that the "shear planes" cut the ReO_3-type structure into blocks and give also reason for potential barriers for electron transport across. This further implies that the doped carriers are confined to the blocks.

In the earlier studies [8, 9] two charge carrier systems were considered to exist simultaneously above the metal–insulator transition, viz. small polarons and quasi-free carriers. Two additional arguments for the appearance of polarons can be put forward. The description of the electronic properties in the present structure type can be done within the framework of the tight-binding theory by $J_{\parallel}/J_{\perp} \gg 1$ with $J_{\parallel}$ and $J_{\perp}$ as the electron transfer amplitudes parallel and perpendicular to the *y*-axis, respectively. When including electron-phonon interaction into the tight-binding picture, the resulting states are large and small polarons for the $J_{\parallel}$ and $J_{\perp}$ direction, respectively [11]. Secondly, the block oxide systems possess superstructures in the $x-z$ plane equivalent to modulated structures in two dimensions (with modulation periods k_x, $k_z = 2\pi/3, \ldots, 2\pi/5$). Accordingly, the Brillouin zone is split into subbands with smaller bandwidths in the plane perpendicular to the *y*-axis. In this case small polaron formation is favoured. It is also known from theoretical considerations that modulated structures have a strong tendency to generate localized states [12]. The large anisotropy of the reflectivity supports the idea that both small and large polaron aspects are present. The interesting question is whether the hopping charge carriers and the carriers responsible for metallic properties can be associated with different or the same structural units. For a conclusive answer more detailed information about the spatial distribution of the charge carriers is needed.

In summary we have shown for the first time the quasi-one-dimensional electronic behaviour of the binary and ternary Nb–W oxides and have attributed it to the structural block units.

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