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Defect structure and DC electrical conductivity of TiO$_2$-NbO$_2$ solid solution

Song, Inho, Ph.D.
Case Western Reserve University, 1990

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DEFECT STRUCTURE AND DC ELECTRICAL CONDUCTIVITY
OF TiO₂-NbO₂ SOLID SOLUTION

by

INHO SONG

Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy

Thesis Advisor: Dr. Hisao Yamada

Department of Materials Science and Engineering
Case Western Reserve University
January 1990
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DEFECT STRUCTURE AND DC ELECTRICAL CONDUCTIVITY
OF TiO$_2$-NbO$_2$ SOLID SOLUTION

Abstract

by

INHO SONG

The defect structure and the dc electrical conductivity of TiO$_2$-NbO$_2$ solid solution have been studied by using time-of-flight neutron diffraction, Nb K-edge x-ray absorption spectroscopy, and dc electrical conductivity measurement as a function of composition. The oxygen content in the solid solutions was determined using thermogravimetric analysis, and the results of other experiments were analyzed and correlated to establish a defect structure that controls the dc electrical conductivity. The lattice parameters and the interstitial defect occupancy were determined using the Rietveld method applied to neutron diffraction results. The valence and the coordination state of Nb ions were determined through XANES and EXAFS analyses of Nb K-edge x-ray absorption data.

The formation of Nb-Nb pairs postulated by other researchers was directly observed by Nb K-edge EXAFS analysis. The formation of Nb-Nb pairs was also noticed in the results of neutron diffraction analysis and dc electrical conductivity measurement. A conductivity maximum was observed at Nb$_{0.1}$Ti$_{0.9}$O$_2$, after which the conductivity decreases with increasing Nb concentration. The decreasing conductivity with increasing Nb concentration is attributed to the pair formation, by which charge carriers are localized between the two Nb ions.
ACKNOWLEDGMENTS

This work is truly the result of enthusiasm, encouragement, and support of the author’s advisor, Professor Hisao Yamada. It has been the author’s privilege and honor to spend the final period of advanced education under Professor Yamada’s guidance. The author is very much indebted to Professor Terence Mitchell, Professor Pirouz Pirouz, Professor Wendell Williams, Professor Mark DeGuire, Professor Alfred Anderson and Professor Benjamin Segall for invaluable advice and comments.

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<tbody>
<tr>
<td>(a)</td>
<td>Lattice Parameter of (a)-axis</td>
</tr>
<tr>
<td>(c)</td>
<td>Lattice Parameter of (c)-axis</td>
</tr>
<tr>
<td>(E_C)</td>
<td>Energy of Conduction Band Edge</td>
</tr>
<tr>
<td>(E_V)</td>
<td>Energy of Valence Band Edge</td>
</tr>
<tr>
<td>(E_F)</td>
<td>Fermi Energy</td>
</tr>
<tr>
<td>(E_g)</td>
<td>Band Gap Energy</td>
</tr>
<tr>
<td>(E_0)</td>
<td>Threshold Energy</td>
</tr>
<tr>
<td>(k)</td>
<td>Wavevector</td>
</tr>
<tr>
<td>(P_{O_2})</td>
<td>Oxygen Partial Pressure</td>
</tr>
<tr>
<td>(r_{M-O,\text{ Avg}})</td>
<td>Average Interatomic Distance between Metal and Oxygen Ions</td>
</tr>
<tr>
<td>(r_{Nb-O})</td>
<td>Interatomic Distance between Niobium and Oxygen Ions</td>
</tr>
<tr>
<td>(S)</td>
<td>Siemens, ((=\Omega^{-1}))</td>
</tr>
<tr>
<td>(\hbar)</td>
<td>Planck Constant</td>
</tr>
<tr>
<td>(\hbar)</td>
<td>Dirac constant</td>
</tr>
<tr>
<td>(k)</td>
<td>Boltzmann Constant</td>
</tr>
<tr>
<td>(\lambda)</td>
<td>Wavelength</td>
</tr>
<tr>
<td>(\rho)</td>
<td>Density</td>
</tr>
<tr>
<td>(\sigma)</td>
<td>Electrical Conductivity</td>
</tr>
<tr>
<td>(\sigma_{ESD})</td>
<td>Estimated Standard Deviation</td>
</tr>
<tr>
<td>(\sigma_{DW})</td>
<td>Debye-Waller Factor</td>
</tr>
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<table>
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<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>a/o</td>
<td>Atomic Percent</td>
</tr>
<tr>
<td>BFBT</td>
<td>Best Fit Based on Theory</td>
</tr>
<tr>
<td>EXAFS</td>
<td>Extended X-ray Absorption Fine Structure</td>
</tr>
<tr>
<td>FABM</td>
<td>Fine Adjustment Based on Model</td>
</tr>
<tr>
<td>IPNS</td>
<td>Intense Pulsed Neutron Source</td>
</tr>
<tr>
<td>LT</td>
<td>Low Temperature</td>
</tr>
<tr>
<td>m/o</td>
<td>Molar Percent</td>
</tr>
<tr>
<td>NSLS</td>
<td>National Synchrotron Light Source</td>
</tr>
<tr>
<td>sccm</td>
<td>Standard Cubic Centimeter per Minute</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>TOF</td>
<td>Time of Flight</td>
</tr>
<tr>
<td>w/o</td>
<td>Weight Percent</td>
</tr>
<tr>
<td>XANES</td>
<td>X-ray Absorption Near Edge Structure</td>
</tr>
<tr>
<td>XAS</td>
<td>X-ray Absorption Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
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</table>
I. INTRODUCTION

TiO$_2$ has received much attention since the discovery of the photocatalytic effect by Fujishima and Honda.$^1$ Many reports have shown that the efficiency of solar energy conversion improves by adjusting the optical band gap of the semi-conducting electrode to the energy (2.4 eV or 510 nm) that corresponds to the peak intensity of the solar spectrum at air mass 1.$^{2-24}$ Among the variety of materials studied for photoelectrodes, the TiO$_2$–NbO$_2$ solid solution has shown an excellent photoelectrochemical stability and an easy tunability of the optical band gap for maximum utilization of solar energy.$^{25}$ In parallel with the effort for technological advancement, much of the basic research has been done to identify the defect structure of TiO$_2$; but NbO$_2$ itself has been understood to a lesser extent, and this is particularly true for the solid solutions. The objective of the present research is to investigate the defect structure of the binary TiO$_2$–NbO$_2$ solid solution and to establish a correlation between the defect structure and the dc electrical property.

Crystal Structure

The structure of TiO$_2$ is shown in Figure 1. Each cation (Ti$^{4+}$) is octahedrally coordinated by anions (O$^{2-}$), and the unit cell contains two TiO$_2$ molecules. The unit cell consists of a body-centered tetragonal titanium sublattice. The oxygen ions are located between titanium (Ti$^{4+}$) ions in alternating face-diagonal directions normal to the c-axis. Thus, the structure can be visualized as being made up of TiO$_6$ octahedra that share edges and corners such that each oxygen ion belongs to three neighboring octahedra. The resulting chain layers (–Ti–O–O–Ti–O–O–) are oriented perpendicular to the c-axis and are extended in
Figure 1. Rutile (TiO$_2$) structure. Three parameters describe the structure: (1) $a$-parameter; (2) $c$-parameter; and (3) $u$-parameter, i.e., the position parameter of oxygen.
consecutive -A-B-A-B- planes normal to each other. The repeat distance of the chains in a plane is \( a/\sqrt{2} \); the separation distance and the longitudinal displacement of neighboring chains are \( a/\sqrt{2} \); and the vertical repeat distance is \( c \). Since the vertical distance \( c \) between the corresponding oxygen ions of neighboring A- (or B-) planes is larger than the O-O separation in a chain, the oxygen octahedron is distorted by a slight stretch in the chain direction of the titanium ion and by compression of the oxygen square normal to the chain and c-axis. This makes the angle O-Ti-O (bisected by c-axis) smaller than its supplement. By chain construction, a zigzag structure of -Ti-O-Ti-O- chain can also be traced. The chain set (based on the B-cations) is crosslinked by A-cations and is turned by 90 degrees against the other chain set (based on the A-cations) crosslinked by B-cations. This implies that each oxygen ion is coordinated by three titanium ions. Thus, while the octahedral construction is such that each titanium ion is shared by six oxygen ions as nearest neighbors, the crystal can also be visualized as being composed of flat, triangular Ti\(_3\)O coordinations.

The structure of NbO\(_2\) is somewhat complicated. It has been reported that NbO\(_2\) at room temperature has a deformed rutile structure, and it transforms to the basic rutile structure at 1073 K upon heating.\(^{26-33}\) In the low temperature (LT) form of NbO\(_2\), one structural unit cell contains 32 formula units, and there are the same type of NbO\(_6\) octahedra sharing edges and corners as those in the rutile type arrangement. Along the c-axis, as shown in Figure 2, cation-cation (Nb-Nb) separations are alternately short and long (2.8 and 3.2 \( \text{Å} \)), and this has been confirmed by many workers using XRD and neutron diffraction techniques.\(^{31, 34-36}\) Sakata\(^{36}\) attributed the alternating cation separations and the distortion of NbO\(_6\) octahedra to the formation of strong covalent pair-bonds (Nb-Nb bonds), along the c-axis. By neutron diffraction experiments Cheetham and Rao determined atomic coordinates in NbO\(_2\) structure,\(^{37}\) and the bond distances are listed in Table 1. The
Figure 2. Deformed rutile (NbO$_2$) structure. The alternating Nb-Nb distance is shown in the right hand side column.
<table>
<thead>
<tr>
<th>Origin</th>
<th>Neighbor</th>
<th>Distance</th>
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<tbody>
<tr>
<td>Nb 1</td>
<td>O 1'</td>
<td>2.10</td>
</tr>
<tr>
<td>Nb 1</td>
<td>O 2</td>
<td>1.93</td>
</tr>
<tr>
<td>Nb 1</td>
<td>O 2'</td>
<td>2.18</td>
</tr>
<tr>
<td>Nb 1</td>
<td>O 3'</td>
<td>2.02</td>
</tr>
<tr>
<td>Nb 1</td>
<td>O 4</td>
<td>2.04</td>
</tr>
<tr>
<td>Nb 1</td>
<td>O 4'</td>
<td>2.01</td>
</tr>
<tr>
<td>Nb 1</td>
<td>Nb 2</td>
<td>2.74</td>
</tr>
<tr>
<td>Nb 1</td>
<td>Nb 2'</td>
<td>3.26</td>
</tr>
<tr>
<td>Nb 2</td>
<td>O 1</td>
<td>2.02</td>
</tr>
<tr>
<td>Nb 2</td>
<td>O 1'</td>
<td>2.06</td>
</tr>
<tr>
<td>Nb 2</td>
<td>O 2'</td>
<td>2.11</td>
</tr>
<tr>
<td>Nb 2</td>
<td>O 3</td>
<td>1.93</td>
</tr>
<tr>
<td>Nb 2</td>
<td>O 3'</td>
<td>2.23</td>
</tr>
<tr>
<td>Nb 2</td>
<td>O 4</td>
<td>2.03</td>
</tr>
</tbody>
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LT form of NbO$_2$ is characterized by a series of superlattice reflections. The diffraction pattern consists of strong lines due to the basic rutile type substructure and of weak ones due to the superstructure. It should be noted that the xz-plane in NbO$_2$ of LT form corresponds to the (110) plane in basic rutile structure. This can be described in the following form:

$$a_1^{LT} = 2 (a_1^R - a_2^R), \quad a_2^{LT} = 2 (a_1^R + a_2^R), \quad a_3^{LT} = 2 a_3^R,$$  \hspace{1cm} (1)

where $a_1^{LT}$ and $a_1^R$ denote lattice translation vectors of the deformed and the basic rutile structures, respectively.

**Nonstoichiometry and Electrical Conductivity**

TiO$_2$, when nonstoichiometric, is an oxygen deficient n-type semiconductor; however, the controversy and question has always been whether anion vacancies or cation interstitials are predominant. Furthermore, the analysis becomes very complicated when the system under investigation involves aliovalent cations whose charges differ from that of host lattice ions. These cations create species with non-zero effective charge and present many possible ways to balance the charge differences. In the following, the nonstoichiometry and defect structure of TiO$_2$, NbO$_2$, and TiO$_2$-NbO$_2$ are reviewed. The defect notations are after Kröger and Vink.$^{38}$

It has been commonly suggested that the defect in TiO$_2$ consists primarily of oxygen vacancies,$^{39-43}$ based on optical absorption, electrical conductivity, and TGA experiments. Much evidence has also been found for titanium interstitials by measuring electrical conductivity, chemical diffusivity, and electron paramagnetic resonance (EPR).$^{44-50}$ Kofstad$^{51}$, however, suggested an equal influence of oxygen vacancies and titanium interstitials. He described that the titanium interstitial is a major type of defect at high temperature and low Po$_2$ conditions.
(this often results in a large deviation from stoichiometry), but the oxygen vacancy becomes a predominant one at low temperature and high \( \text{Po}_2 \). This seems consistent with the way that the Magnéli phase (a series of \( \text{Ti}_n \text{O}_{2n-1} \) phase, where \( n \) is an integer; also known as a homologous series) is formed. At low \( \text{Po}_2 \) oxygen vacancies are formed, but their concentration is yet too low to coalesce; that is, a large contribution of configurational entropy of the point defect prevents the formation of vacancy aggregates. If the concentration of oxygen vacancies is increased further by lowering \( \text{Po}_2 \), the vacancies start to precipitate and form a planar defect structure: this simulates a missing plane of oxygen along a particular crystallographic orientation and is called a crystallographic shear (CS) plane in that this type of defect structure can be viewed as if it results from a mechanical shear transformation. This implies that at some point the activity of oxygen vacancies must decrease with a further decrease in oxygen partial pressure, and thus the interstitial titanium becomes predominant at low oxygen partial pressure. A similar argument can be applied to the formation of CS planes by the capturing of interstitial titanium ions at high temperature. If this approach is correct, the next question regards the ionization states of the vacancies and interstitials.

Ait-Younes et al.\textsuperscript{52} estimated the effective charge of cation in nonstoichiometric \( \text{TiO}_2 \) by measuring the stationary chemical potential gradient of oxygen at 1323 K (actual \( \text{Po}_2 \) was not specified, but it seems \( \text{Po}_2 < 10^{-13} \text{ atm} \)). Using Wagner's formalism,\textsuperscript{53} they first calculated values of electromigration coefficients for \( \text{Ti}^{***} \), \( \text{Ti}^{**} \), \( \text{V}_{\text{O}}^{**} \), and \( \text{V}_{\text{O}}^{*} \); and then compared those with the experimental results. The comparison indicated that at 1323 K the \( \text{Ti}^{***} \) is the majority defect in the bulk and that the \( \text{Ti}^{**} \) is a negligible constituent. This behavior seems independent of anion nonstoichiometry. Marucco et al.\textsuperscript{54} based on TGA results, suggested a transition of the type of predominating defect from \( \text{V}_{\text{O}}^{**} \) to \( \text{V}_{\text{O}}^{*} \), with increasing \( \text{Po}_2 \). They concluded that oxygen vacancies (either \( \text{V}_{\text{O}}^{**} \) or \( \text{V}_{\text{O}}^{*} \), or both)
are predominant at low temperature, and titanium interstitials (Ti\(^{***}\)) at high temperature (above 1173 K). The temperature, 1173 K, is probably the limit of thermodynamic stability above which a crystallographic adjustment (such as condensation of anion vacancies and formation of CS planes) has to arise in order to accommodate the increase in configurational entropy. This idea needs to be supported by a dynamic TGA experiment done simultaneously with an XRD measurement. Later, Marucco et al.,\(^{55}\) using TGA technique, reported that with a small deviation from stoichiometry V\(^{**}\)\(_O\) is the major type of defect, whereas for a large amount of nonstoichiometry either V\(^*\)\(_O\) or Ti\(^{***}\) predominates. Also, they suggested an intermediate region where all three (V\(^*\)\(_O\), V\(^{**}\)\(_O\), and Ti\(^{***}\)) are coexisting and active. According to Blumenthal and Whitmore,\(^{56}\) there is a biphasic region that defines the lower limit (TiO\(_{1.998}\)) of nonstoichiometry in TiO\(_2\) and the upper limit (TiO\(_{1.992}\)) of the Magnéli phase. This is consistent with the process that the CS plane is formed. However, if the intermediate region indicated by Marucco et al. actually corresponds to the biphasic region of Blumenthal and Whitmore, then the major defect in nonstoichiometric TiO\(_2\) has to be V\(^{**}\)\(_O\).

Ero\(^{57}\) determined the solubility of Nb\(^{5+}\) in TiO\(_2\) in air, and the range of homogeneity. The range of homogeneity means the maximum allowed deviation from stoichiometry before the Magnéli phase starts to emerge. Up to the solubility maximum, approximately 8 a/o at 1333 K, the range of homogeneity increases proportionally with the dopant concentration. He suggested that the donor dopants (e.g., Nb\(^{5+}\)) are electronically compensated by additional oxygen uptake in the oxidized state. This type of compensation mechanism operates such that the negatively charged electronic defects neutralize the positive side of the electroneutrality condition (dominated by Nb\(^{5+}\) donor dopant) and is independent of equilibrium oxygen activity. On the other hand, the donor dopant can be compensated by the creation of charged point defects, and this mechanism (often
referred to as self-compensation mechanism) also makes the electronic defect concentration independent of oxygen activity.

Marucco et al.,$^{55}$ using TGA, reported relations between the oxygen partial pressure and the amount of nonstoichiometry in TiO$_2$, NbO$_2$, and the solid solution. They suggested that in TiO$_2$ the main defects are the oxygen vacancy ($V'_O$ or $V''_O$) and titanium interstitial (Ti$^{**}$), while in NbO$_2$ the $V'_N$ prevails. The solid solution (Nb$_x$Ti$_{1-x}$O$_2$) showed a somewhat complicated result: with $X$ greater than 0.96, the behavior is analogous to that of NbO$_2$; whereas with $X$ less than 0.96 the solid solution exhibits either metal or oxygen deficiencies depending on the Po$_2$. Their study on Nb$_{0.005}$Ti$_{0.995}$O$_2$ suggested that anion vacancies ($V'_O$ or $V''_O$) are the main defects in the oxygen deficient domain, while cation vacancies ($V'''_{Ti}$) are the main defects in the metal deficient domain. Also, they suggested that the intrinsic defects in TiO$_2$ are Schottky ($V'''_{Ti} + 2V''_O$) rather than Frenkel ($V'''_{Ti} + Ti''''$) pairs.

Valigi et al.$^{58}$ measured the maximum solubility of Nb$^{5+}$ into TiO$_2$ and suggested that the introduction of Nb$^{5+}$ ions are compensated by the creation of an equivalent amount of Ti$^{3+}$ within the solubility limit (approximately 6.2 a/o). However, they suggested that upon subsequent heating in air the Ti$^{3+}$ ions are oxidized to Ti$^{4+}$, and this results in the creation of complementary cation vacancies that are used for neutralization of the Nb$^{5+}$ ions. They also reported a presence of Ti$^{3+}$ from EPR and IR diffuse reflectance experiments and suggested a possibility of Ti$^{3+}$-Ti$^{3+}$ pair formation with increasing Nb concentration.

Shin et al.$^{59}$ reported that the structural distortion in TiO$_2$-NbO$_2$ starts to arise when $X$>0.73. Sakata$^{60}$ also reported the structural distortion, but only within the range of $X$>0.85. She showed that the lattice parameter along the a-axis increases linearly with increasing $X$, while that along the c-axis remains almost unchanged at roughly $X$>0.4. Also, Sakata$^{60}$ showed that the alternating Nb-Nb
distances along the c-axis merge to a single value, 0.3 nm, at X=0.7. It appears that the short Nb-Nb distance (e.g., 0.28 nm at X=1) is comparable to the nearest neighbor distance of niobium metal, 0.286 nm. However, the directionality of the bonding along the c-axis suggests a bonding with a covalent nature rather than a metallic one.

Poumellec and Marucco\textsuperscript{61} measured the electrical conductivity and the thermoelectric power in Nb\textsubscript{x}Ti\textsubscript{1-x}O\textsubscript{2} (0.04<X<1). The result showed a negative coefficient of thermoelectric power for all compositions, indicating that the solid solution is an n-type conductor. The result also showed that the electrical conductivity at room temperature decreases with increasing Nb concentration (X>0.1). However, another study by Poumellec et al.\textsuperscript{62} showed that the electrical conductivity at room temperature increases with increasing Nb concentration (0.005<X<0.04). The combined results of Poumellec and Marucco\textsuperscript{61} and Poumellec et al.\textsuperscript{62} suggest that there exists a conductivity maximum between X=0.04 and X=0.2.

Poumellec et al.\textsuperscript{63} reported a partial transfer of Nb 4d-electrons onto the Ti 3d-orbital from the analysis of XANES of Ti K-edge, implying that the Ti 3d and Nb 4d levels are at the same energy. The result also showed that the absorption spectra shift to lower energy with increasing Nb concentration. They attributed this shift to the increasing tendency of the formation of Ti\textsuperscript{3+} with increasing Nb concentration. This is in agreement with Valigi et al.\textsuperscript{58} Unfortunately, very few reports are available regarding the XANES of TiO\textsubscript{2}-NbO\textsubscript{2} solid solutions. This is because it has not been very long since people started to realize that there is much useful chemical information contained in the near-edge structure. Also, in most of the cases experimental facilities were probably not readily available with the resolution (<1 eV) required for a meaningful XANES analysis.

\textbf{Scope of Research}

The present research consists of four parts. In the first part, the TiO\textsubscript{2}-NbO\textsubscript{2}
solid solutions of various composition are synthesized. In the second part, the solid solutions are characterized by means of XRD, neutron diffraction, XAS (XANES and EXAFS), and TGA. In the third part, dc electrical conductivity measurements are conducted. In the fourth part, the results are analyzed and correlated with each other.

It is known that TiO\textsubscript{2} and NbO\textsubscript{2} form a substitutional solid solution over the entire range of composition. This, however, can be achieved only under a reducing condition, because NbO\textsubscript{2} tends to form Nb\textsubscript{2}O\textsubscript{5} in air and thereby turns the solid solution into a two-phase mixture (TiO\textsubscript{2} and TiO\textsubscript{2}•Nb\textsubscript{2}O\textsubscript{5}, TiO\textsubscript{2}•Nb\textsubscript{2}O\textsubscript{5} and TiO\textsubscript{2}•3Nb\textsubscript{2}O\textsubscript{5}, or TiO\textsubscript{2}•3Nb\textsubscript{2}O\textsubscript{5} and Nb\textsubscript{2}O\textsubscript{5}). Thus, the oxygen partial pressure should be low enough to maintain the oxidation state of Nb ions at 4+, but it should not be too low to prevent the formation of lower oxides (e.g., NbO, TiO, Magnéli phase, etc.).

The range of composition to be studied, including TiO\textsubscript{2} and NbO\textsubscript{2}, is 10–90 molar percent (m/o) of NbO\textsubscript{2} in TiO\textsubscript{2} at an increment of 10 m/o. In addition, attention is given to 32 m/o NbO\textsubscript{2} solid solution for a reason to be explained shortly. The specimens are first examined by XRD to confirm that the solid solution is a single phase, and to determine the lattice parameters. Generally, XRD study provides useful crystallographic information about the cation sublattice in many metal oxides. Unfortunately, however, the XRD technique is not suitable for the detection of a minute change in the anion sublattice because of the low x-ray scattering factor of oxygen. This means that any small change in anion substructure may not be detected by XRD unless there is a major crystallographic reconstruction.

On the other hand, the neutron diffraction technique generally tells more details about the anion substructure because in many cases the neutron scattering lengths of cations and anions are not too much different. Also, since the atomic
scattering factor stays constant with respect to $\sin \theta/\lambda$ in the time-of-flight (TOF) neutron diffraction technique, quantitative analyses of peak profile and intensity is possible. The details of the TOF technique are described in the following chapter. For TiO$_2$-NbO$_2$ substitutional solid solution, the neutron diffraction technique is specially advantageous. This is because the neutron scattering length of Ti is negative ($-0.33 \times 10^{-12}$ cm), while that of Nb is positive ($0.71 \times 10^{-12}$ cm). At a special composition (roughly 32 m/o NbO$_2$), the contributions of cations to the neutron scattering are expected to cancel out, providing that all cations are randomly distributed in the cation sublattice. Therefore, it is thought that the neutron scattering experiment would present more information about the anion sublattice and might reveal a possible ordering of point defects (e.g., ordering of interstitial cations) in the solid solution. In addition to 32 m/o NbO$_2$ solid solution, the composition is extended to 10, 25, 40, 50, 60, 70 and 80 m/o NbO$_2$ to examine how the defect structure would change with respect to composition.

Despite the great interest in defect structure of TiO$_2$-NbO$_2$ solid solution, very little has been reported about the oxidation and coordination state of specific cations such as Nb and Ti in the bulk. This is because of very limited availability of analytical techniques that discriminate individual constituents in the bulk. In the past decade, however, the XAS (XANES and EXAFS) has been used extensively to probe the chemical state and the coordination environment of many chemical compounds.$^{64-66}$ The XAS is an element-specific bulk technique, with which the behavior of a selected element in the bulk is observed regardless of crystallinity. In the present research the element Nb is chosen, and the behavior of the Nb ion is studied by Nb K-edge absorption spectra. The Nb K-edge is chosen because no study has been done at the Nb K-edge, and because the experimental facilities (Beamline X-18B, National Synchrotron Light Source at Brookhaven National Laboratory) are capable of providing the necessary resolution for XANES analysis.
Through the XANES analysis, the oxidation and the coordination states of Nb ions are determined, and through the EXAFS analysis, the interatomic distance and the coordination number of the first coordination shell are determined. The XAS is an element-specific technique, whereas the neutron diffraction technique is a site-specific one. Thus, the results of the two experiments are expected to be highly complementary to each other. For example, while the interatomic distance determined from neutron diffraction data is the mean distance between metal (i.e., there is no distinction between Nb and Ti) ions and oxygen ions, the distance determined from the XAS data is the true distance between Nb and O ions.

In order to interpret the defect structure correctly from the results of the analyses of neutron diffraction and XAS data, and to correlate these results with the dc electrical conductivity, it is important that the amount of nonstoichiometry be determined with accuracy. In order to achieve this, a TGA technique is used. The weights of the specimen before and after oxidation are measured, and the amount of nonstoichiometry is calculated from the weight change. In practice, however, there are some technical difficulties that may induce serious errors. The weight change measurements can be done in two different ways: in situ and ex situ. The in situ measurement is generally used in that the weight of specimen can be continuously measured during the oxidation process, but this technique is undesirable in the present research because of a buoyancy effect that perturbs the measurement of accurate weight. The ex situ method, on the other hand, measures only the initial and the final weights of the specimen, but this method is also very much susceptible to error due to the adsorption of moisture from the environment during the weight measurement. In the present research the ex situ technique is used because it is more important to obtain the accurate weight than to know the onset of oxidation.
II. EXPERIMENTAL PROCEDURE

The present research consisted of the following experiments: synthesis of TiO$_2$–NbO$_2$ solid solution; characterization of solid solution by XRD, neutron diffraction, XAS (XANES and EXAFS), and TGA; and measurement of dc electrical conductivity.

**Preparation of Solid Solution**

Solid solutions, Nb$_x$Ti$_{1-x}$O$_2$, of various $X$ were synthesized from mixtures of TiO$_2$ (Alfa Products, 99.8 % pure, metals basis) and NbO$_2$ powders by solid state sintering. The NbO$_2$ was fabricated from Nb$_2$O$_5$ (Johnson Matthey, 99.9999% pure, metals basis) by a reduction process to be described below.

For the reduction of Nb$_2$O$_5$ and the synthesis of solid solution, a molybdenum disilicide furnace (Lindberg, type 55434) muffled with an alumina tube (Coors, AD998 grade, 3 inch outside diameter) was used. The temperature was measured by a type-R thermocouple with a digital thermometer (Fluke, model 2190A) and was controlled by a programmer (Gulton, model West 2050).

In order to minimize contamination during the reduction and synthesis, TiO$_2$ crucibles were used. The crucibles were prepared by an aqueous slip casting technique. Plaster molds for slip casting were obtained from Duncan Ceramics. Starch powder (Johnson and Johnson, Baby Powder) was used as a mold releasing agent. The formula for slip casting is listed in Table 2.

The NbO$_2$ powder was produced from Nb$_2$O$_5$ powder in a reducing atmosphere at 1450°C. The atmosphere consisted primarily of argon (Air Products, Ultra-Pure Carrier grade) purified by using a titanium-charged oxygen-getter (Centorr, Inert Gas Purifier/Analyzer, model 2A). After the purification, 5 v/o
**TABLE 2**

*Slip Casting Formula for Fabrication of TiO₂ Crucible*

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O (pH = 9)</td>
<td>220 cc</td>
</tr>
<tr>
<td>TiO₂ (&lt; 1 micron)</td>
<td>400 g</td>
</tr>
<tr>
<td>Tannic Acid</td>
<td>0.4 g</td>
</tr>
<tr>
<td>Darvan C</td>
<td>1 g</td>
</tr>
<tr>
<td>TBP</td>
<td>0.3 g</td>
</tr>
<tr>
<td>Firing Temperature</td>
<td>1500 °C</td>
</tr>
<tr>
<td>Firing Time</td>
<td>2 hr</td>
</tr>
</tbody>
</table>
hydrogen (Air Products, Ultra-Pure Carrier grade) was mixed with it as a reactive species. The flow rate of the gas mixture was 1000 sccm per 75 g of Nb₂O₅. The gas mixing and flow controls were done by using mass flow controllers (MKS, model 259B). The heating and cooling rates were 210 degrees per hour, and the temperature was held at its maximum (1450°C) for 5 hours. Upon completion of each reduction process, the powder was examined by XRD to confirm the NbO₂ single phase.

Solid solutions (NbₓTi₁₋ₓO₂) of various X were prepared by isostatically pressing and sintering the mixtures of TiO₂ and NbO₂. Since NbO₂ tends to react with TiO₂ at an elevated temperature in air to form TiO₂·Nb₂O₅ or TiO₂·3Nb₂O₅, a reducing atmosphere was used for the syntheses of solid solutions. The atmosphere was identical to that used for the fabrication of NbO₂ powder (5 v/o hydrogen mixed with purified argon).

To achieve homogeneity, the powder mixture was milled for 24 hours in methanol (EM Science, GR grade) using zirconia grinding media (Toyo Soda, YZT milling media). The mixture was dried in a rotary vacuum vaporizer (Büchi, Rotavapor model RE121) at 30°C. The dried powder mixture was isostatically pressed at 30,000 psi and was sintered at 1400°C for 5 hours. The synthesized solid solution was ground and sieved down to less than 150 μm (equivalent to 100 mesh) using agate mortar and pestle; and the coarse powder was milled in methanol for 24 hours using yttria-stabilized-zirconia balls. The milled slurry was dried in the rotary vacuum vaporizer at 30°C.

The synthesized powder, roughly 50 g, was enclosed in a graphite die (Poco Graphite, HPD-3, 2 inch inside diameter) lined with graphite foil (Union Carbide, Grafoil, GTA Grade), and the die was loaded into a hot press (Centorr Associates). The hot pressing chamber was evacuated to less than 10⁻⁴ atm and was purged with the purified argon, and this procedure was repeated twice. The hot pressing was
performed following a schedule shown in Figure 3. At the onset of densification at 1250°C, the control program for hot pressing was paused, and the axial shrinkage of the specimen was monitored. Upon completion of the densification, the program was restarted to cool down. The pressure applied was 3000 psi, the heating rate 1000 degrees per hour, the cooling rate 500 degrees per hour, and the pressing rate 500 psi per hour.

After the hot pressing, the density was measured by using the buoyancy technique. The measurement was done in deionized water (density = 0.9978 g/ml) at 295 K using an electronic balance (Mettler, AE163) with density determination kit (Mettler, ME-40290). The buoyancy due to air was not taken into consideration; but, if considered, the true densities would have been approximately 0.001 g/cm³ more than those without the correction. Prior to measurements, the specimens were carefully cleaned with acetone (EM Science, GR grade) in an ultrasonic cleaner (Branson, model 2200).

**Characterization of Solid Solution**

The solid solutions synthesized and hot pressed were characterized using various techniques. The XRD technique was used to ensure the phase homogeneity in the synthesized solid solution. The neutron diffraction and XAS experiments were conducted to identify the type and structure of defects in the hot pressed solid solution.

**X-ray Diffraction**

In order to ensure the single rutile phase in the solid solution, the crystal structure and the lattice parameters were determined by powder XRD technique. The measurement was done at room temperature using an automated x-ray diffractometer (Scintag, model PAD V). The system consisted of an x-ray source (Cu target, 45 kV and 40 mA), a goniometer (250 mm radius), a divergence slit (2 mm),
Figure 3. Hot pressing schedule used for preparing $\text{Nb}_x\text{Ti}_{1-x}\text{O}_2$ solid solutions.
scatter slits (4 mm at tube side, and 0.5 mm at diffracted beam side), a receiving slit (0.3 mm), a soller slit, and a detector (Peltier, Solid State Detector tuned to Cu Kα₁). A zero background quartz plate (cut 6 degrees off the c-axis) was used as a specimen holder. As an internal standard, KBr (JCPDS 36-1471) or KCl (JCPDS 4-587) was used depending on the position of the solid solution peaks. With the corrected d-spacings, tentative lattice parameters corresponding to each Bragg reflection were calculated. These tentative parameters were then plotted against an extrapolation function, cos²θ/sinθ. The extrapolation was done using the least square method. Although the data were corrected and were treated using the least square method, neither the accuracy nor the precision is claimed here. The reasons are: firstly, the 2θ range was only from 20 to 100 degrees; secondly, the step size was only 0.05 degrees that would, at its best, impose an inevitable uncertainty of the order of 5000 parts per million for a-parameters; and thirdly, as reported by Valigi et al., the lattice parameter may change with nonstoichiometry. Thus, the information obtained from XRD was used solely for the purpose of phase identification during the sample preparation stage.

**Neutron Diffraction**

Time-of-flight (TOF) neutron diffraction experiments were conducted at the Intense Pulsed Neutron Source (IPNS), Argonne National Laboratory. In the TOF technique the positions of source, specimen, and detector are fixed in contrast to the thermal neutron diffraction or XRD experiment in which the detector moves about the specimen. Consequently, the only independent variable in the Bragg equation is the wavelength. This wavelength is determined by measuring the TOF of neutron from a chopper to a detector, and by converting the TOF to the wavelength using the de Broglie relation. The data are binned in 5 μsec intervals. Typically, the wavelength ranges from 0.6 to 4 Å, and the spectrum is of gaussian shape. The speed of the pulsed neutrons are of the order of 100 km/sec.
The compositions of TiO$_2$-NbO$_2$ solid solutions studied were 10, 25, 32, 40, 50, 60, 70, and 80 m/o NbO$_2$ in TiO$_2$. The oxygen content of the solid solution was determined thermogravimetrically by measuring the weight gain during oxidation at 1025°C. The oxygen contents were later used as a constraint for structural refinement. The TOF neutron diffraction data were collected from two backscattering detector banks at 2θ=150 degrees, as these detector banks provide the highest resolution. Roughly 10 g of powder specimen was used in each experiment and was enclosed in a half inch diameter seamless vanadium tube. The raw data were analyzed computationally by using the Rietveld method, and the procedure was divided largely into two steps: profile preparation, and structural refinement. In the profile preparation step, the incident spectrum was first fitted to the following series expression for intensity, and a correction factor was calculated for each reflection:

\[ I_1 = A_0 + A_1 \exp(-A_2 T) + A_3 \exp(-A_4 T^2) + A_5 \exp(-A_6 T^3) + A_7 \exp(-A_8 T^4), \]  

(2)

where $A_1$, $A_2$, $A_3$, $A_4$, $A_5$, $A_6$, $A_7$, and $A_8$ are constants, and $T$ represents the time-of-flight. This procedure was repeated until the agreement factor was minimized, by adjusting the cell parameters of a model structure. The agreement factor ($R_w$) to be minimized is given by

\[ R_w = \sum \frac{w_i (y_i - y_{ci})^2}{}, \]  

(3)

where $w_i = 1 / y_i$,

$y_i$ = observed intensity at $i^{th}$ step,

$y_{ci}$ = calculated intensity at $i^{th}$ step,

and the summation is taken over all data points. At the end of the computation,
the lattice parameters, background parameters, peak profile parameters, and a scale factor were obtained.

In the structural refinement step, the following parameters were further refined: a positional parameter for oxygen ions at \((u,u,0)\), anisotropic thermal parameters for oxygen ions, and an occupancy factor for the regular cation site at \((0,0,0)\). Additionally, occupancy factors were also refined for octahedral interstitial sites at \((0.5,0,0.5)\) and tetrahedral interstitial sites at \((0.135,0.135,0.5)\). The refinement was constrained to reflect the metal/oxygen ratio determined by TGA; i.e., the sum of the occupancies of the regular cation sites and that of the interstitial sites were constrained to be equal to the measured stoichiometry. The only positional parameter allowed to vary was that of oxygen at a special position \((X,X,0)\). The scattering length of the regular cation site at \((0,0,0)\) was allowed to vary, and the occupancies were calculated based on the total scattering length. The scattering lengths of cations used for refinement were \(0.71 \times 10^{-12}\) cm for niobium, and \(-0.33 \times 10^{-12}\) cm for titanium.

At the end of refinement cycle, the standard deviation was estimated from the formula,

\[
\sigma_{\text{ESD}} = \left[ M_{ii}^{-1} \Sigma_i (y_i - \bar{y})^2 / (N - P + C) \right]^{1/2},
\]

where \(M_{ii}^{-1}\) is the corresponding diagonal element, \(N\) is the number of observations, \(P\) is the number of parameters being refined, and \(C\) is the total number of constraints.

**Thermogravimetry**

The nonstoichiometry of solid solution was determined by *ex situ* TGA. The experiment was carried out by oxidizing the hot pressed specimens in air (Air Products, Zero grade). The amount of nonstoichiometry was calculated from the
weight change. One assumption in the calculation, however, was that the specimens attained perfect stoichiometry after oxidation.

In principle, the in situ TGA allows more understanding of the oxidation process such as the onset temperature of oxidation. However, because of the extreme difficulty of measuring the true weight in the presence of buoyancy and convection effects, the ex situ method was used in the present research. In this technique only two measurements are required: the initial and the final weights of the specimen. A difficulty, however, was to mitigate the effect of humidity. In order to minimize the error, or rather to be consistent, the humidity inside the balance (Mettler, model AE163) was maintained at 70 $\mu$g maximum of water per 1 litter of air at 25°C using a large amount of calcium sulfate (Hammond, Drierite) crystals. The balance was calibrated before each measurement using a calibration weight (Mettler, class S, 100 g $\pm$ 200 $\mu$g). The stabilization and the integration times for measurement were 8 and 12 seconds, respectively. Since this configuration provided the reproducibility of $\pm$30 $\mu$g, and the expected increase in weight ranges approximately 1-6 % from TiO$_2$ to NbO$_2$, the resolution in oxygen content is expected to be in the range from $\pm$0.003 to $\pm$0.0005, respectively. In order to ensure precision, the weight was measured six times, and these were averaged. In addition, the experiment was repeated three times per composition, and the results were again averaged.

Before starting each set of experiments a platinum crucible was ultrasonically cleaned in acetone and was baked at 1400°C for 2 hours for removal of organic residue. After measuring the weight of the crucible, approximately 1 gram of specimen was loaded into the crucible, and the true weight of the specimen was determined. The specimen was then oxidized in air at 1025°C for 2 hours. After the oxidation, the weight of the specimen was measured, and the net weight gain was determined. Finally, the oxygen content was calculated from the amount of
weight gain. The procedure of the calculation is shown in Table 3.

**X-ray Absorption Spectroscopy**

The specimens for the XAS experiment in transmission mode was prepared so as to yield a unit absorption in the following equation:

\[
\mu x = (\mu / \rho) \rho x, \tag{5}
\]

\[
x = \mu x / [(\mu / \rho) \rho], \tag{6}
\]

\[
x = 1 / [(\mu / \rho) \rho], \tag{7}
\]

where \(\mu\) is the linear absorption coefficient, \(\mu / \rho\) the mass absorption coefficient, \(\rho\) the density of specimen, and \(x\) the thickness of specimen. The ideal thickness was calculated first, and the specimen was prepared accordingly. The calculated thickness and the actual thickness are shown in Figure 4. After completing the XAS experiments, the actual thickness (average of 60 measurements per specimen) was measured by using a digital micrometer with spherical tips (Mitsutoyo).

The x-ray absorption spectroscopy (XAS) experiment was conducted on beam line X-18B at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. The NSLS operating at 2.5 GeV, the storage ring current was approximately at 90–180 mA. The x-ray was monochromated using a channel-cut Si (220) crystal with weak-link. In order to minimize the harmonic content of the incident x-ray beam, the monochromator was detuned to pass approximately 80 % of the incident photon intensity. The slit width was set to 1 mm to attain ±1.0 eV resolution. Thus, specimens were exposed to a 1x10 mm² x-ray beam.

The Nb K-edge x-ray absorption data were collected in ambient conditions in transmission mode, and the energy calibration was maintained to ±1.0 eV by using a niobium foil (25 μm, A.D. MacKay). The incident intensity (\(I_0\)) and the transmitted intensity (\(I_x\)) were measured by using sealed-ion-chamber proportional
TABLE 3

Procedure for Determination of Oxygen Content

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
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<tr>
<td>[Ti]</td>
<td>:</td>
<td>47.90</td>
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<td>[Nb]</td>
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</tr>
<tr>
<td>[O]</td>
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</tr>
<tr>
<td>[Nb₂O₅]</td>
<td>:</td>
<td>265.8098</td>
</tr>
</tbody>
</table>

Reoxidation Reaction:

\[ m(\text{Nb}_x\text{Ti}_{1-x}\text{O}_{2+y}) \longrightarrow m(\frac{x}{2}\text{Nb}_2\text{O}_5 + (1-x)\text{TiO}_2) \]

Measurement of Weight Change

| Initial Weight | \( W_i \) | g |
| Final Weight   | \( W_f \) | g |

Calculation of \# of moles of solid solution in \( W_f \)

Calculation of \( 2+y \)
Figure 4. Variation of ideal and actual thicknesses of specimens used in x-ray absorption spectroscopy experiment.
counters with absorption lengths of 10 cm and 30 cm, respectively. The ion-
chambers were filled with argon gas, and the gas pressures were 1.19 atm for $I_o$
and 1.98 atm for $I_t$. This gave 20% absorption of incident intensity for $I_o$ and the
rest for $I_t$ at 19.074 keV. The data were collected according to the scan parameters
listed in Table 4.

The XAS data were analyzed using a VAX 6800 computer (Digital Equipment
Corp.) and FORTRAN programs employing algorithms from the IMSL
Library (IMSL Inc.) for cubic spline interpolation, evaluation, differentiation, and
smoothing. The data were normalized according to a procedure similar to that
described by Wong et al. The preedge data were modeled with a two-term linear
function, which was fitted below the onset of the absorption edge and extrapolated
above the edge. The postedge data were modeled with a three-term second degree
polynomial, which was fitted above the edge and extrapolated below the edge. The
normalized data were obtained by subtracting the preedge absorption approxima-
tion from the raw data and then dividing the difference by the postedge absorption
approximation. This normalization procedure enabled a direct quantitative
comparison of the shapes and intensities of features found in XANES, and further
it provided normalized EXAFS data with an absorption edge-jump equal to unity.

The XANES was analyzed by taking the first and the second derivatives of
the normalized data in terms of energy. For the numerical differentiation the
Fourier transformation technique by Cameron and Moffatt was used. The
EXAFS data reduction and analysis were performed by using techniques and
procedures described by Téo. The raw data in energy scale (i.e., $\chi(E)$ vs. $E$)
were first converted into $k$-space (i.e., $\chi(k)$ vs. $k$). The conversion was done at
an experimental threshold energy ($E_0$) of 19.000 keV using the following equation:

$$k = \left[ \frac{2m (E - E_0)}{h^2} \right]^{1/2},$$  (8)
### TABLE 4

Scan Parameters in X-ray Absorption Experiment

<table>
<thead>
<tr>
<th>Region</th>
<th>Start</th>
<th>End</th>
<th>Step</th>
<th>Mode</th>
<th>Time (sec)</th>
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<td>18739</td>
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<tr>
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<td>4.000</td>
<td>8.000</td>
<td>0.04</td>
<td>k</td>
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<tr>
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<tr>
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<td>12.040</td>
<td>16.000</td>
<td>0.04</td>
<td>k</td>
<td>10.000</td>
</tr>
</tbody>
</table>

Total Number of Data Points: 451
where \( k \) is the photoelectron wavevector, \( m \) the electron rest mass, \( E \) the incident photon energy, \( E_0 \) the threshold energy for K-shell ejection, and \( \hbar \) Dirac constant. In order to extract EXAFS, i.e., to obtain \( \chi(k) \) vs. \( k \), the postedge background absorption was modeled by using 5 sections (3.123 Å\(^{-1}\) per section) of cubic spline function. The EXAFS, \( \chi(k) \), were weighted by \( k^5 \) and Fourier transformed without phase shift correction to obtain a frequency spectrum called a pseudo radial distribution function (PRDF). In PRDF each peak corresponds to individual sinusoidal frequencies and represents radial coordination shells. By applying a window (Hanning function) to PRDF between 0.91 Å and 2.19 Å, the contribution of the first coordination shell (i.e., the contribution of backscattering by oxygen ions) to EXAFS was isolated and transformed from pseudo radial distance space to \( k \)-space. This step is generally called Fourier filtering.

The Fourier filtered data \((k^2 \chi(k) \text{ vs. } k, 4 \text{ Å}^{-1} \leq k \leq 14 \text{ Å}^{-1})\) were employed in the nonlinear least square curve fitting. The curve fitting iteratively refines the parameters in the following EXAFS equation for backscatterer \( j \) around central atom \( i \):

\[
\chi(k) = \sum_j B_{ij} F_{ij}(k) \exp(-2\sigma_{ij}^2k^2) \exp[-2r_{ij}/\Lambda(k)] \sin[2kr_{ij}+\phi_{ij}(k)] / kr_{ij}^2,
\]

(9)

where \( B_{ij} \) is a scale factor, which is related to the coordination number, \( N_{ij} \), by \( B_{ij} = S_i N_j \) (\( S_i \) is the amplitude reduction factor obtained from the curve fitting of model compound, \( \text{NbO}_2 \) in the present study); \( F_{ij} \) a backscatterer amplitude function; \( \sigma_{ij} \) a Debye-Waller factor accounting for thermal and static disorder; \( r_{ij} \) an interatomic distance; \( \Lambda(k) \) an inelastic electron mean free path; and \( \phi_{ij} \) a total phase shift function. This curve fitting routine implements the single scattering theory of EXAFS,\(^{70}\) and Teo and Lee's plane-wave approximation.\(^{71}\) The theoretical backscatterer amplitude function \( F_{\text{O}}(k) \), absorber phase function \( \phi_{\text{Nb}}(k) \),
and backscatterer phase shifts function $\phi_0(k)$ calculated by Teo and Lee using the Herman-Skillman wave function were used in the curve fitting. The amplitude and phase functions are shown in Figure 5.

In the present study, four parameters were refined according to the best fit based on theory (BFBT) method by Teo et al.: (1) a scale factor, $B$; (2) a Debye-Waller factor, $\sigma$; (3) an interatomic distance, $r$; (4) an energy shift $\Delta E_0$, which is equal to $E_0^{th} - E_0$ ($E_0^{th}$ is the theoretical threshold energy for which $\phi(k)$ is defined). The result of BFBT was further treated by the fine adjustment based on model (FABM) technique developed by Teo et al. The advantage of the FABM technique is that only the characteristic change in threshold energy ($\Delta E_0^*$) needs to be obtained from the model to calculate the interatomic distance ($r_{FABM}^*$) of unknown compounds. Similarly, only the characteristic Debye-Waller factor ($\sigma^*$) and the characteristic amplitude reduction factor ($S^*$) need to be obtained from the model to calculate the coordination number ($N_{FABM}$) in the unknown. Thus, correlations within the two sets of parameters ($\Delta E_0$ vs. $\Delta r$ and $B$ vs. $\sigma_{DW}$) are modeled to yield phase and amplitude correlation curves for each term in Equation X. As a model compound for FABM, NbO$_2$ was chosen because the crystallographic parameters are well characterized, and the bulk chemical state, i.e., valence, is known. Two parameters were adjusted using the FABM technique: interatomic distance and coordination number. Procedures for the interatomic distance FABM and the coordination number FABM are illustrated in Figure 6 and Figure 7, respectively. In coordination number FABM the characteristic Debye-Waller factor was assumed to be approximately equal to the static Debye-Waller factor of the model compound (NbO$_2$) because the contribution of the vibrational term in the total Debye-Waller factor is negligible compared with the static displacement in the model compound.
Figure 5. Theoretical backscattering amplitude functions and phase functions used in Nb K-edge EXAFS analyses: (a) Theoretical backscattering amplitude functions ($F_{Nb}$, $F_{Ti}$, and $F_{O}$) vs. photoelectron wavevector ($k$); (b) Theoretical phase functions (total phase shifts of Nb, Ti, and O with respect to central absorber Nb) vs. photoelectron wavevector ($k$); (c) Total phase difference between Nb and Ti backscatterers vs. photoelectron wavevector ($k$).
Figure 6. Schematic description of FABM distance adjustment. At the known crystallographic distance of the model \((r_m)\) a characteristic \(\Delta E_0^*\) is obtained which is then transferred to the unknown system to yield the distance adjustment \((r_u)\) to the BFBT refined distance at \(\Delta r = 0\). (The figure is taken from Teo et al.\textsuperscript{72})
Figure 7. Schematic description of FABM coordination number adjustment. At the characteristic $\sigma^*$ (determined from model compound) the scale factor $B_m$ is obtained and the amplitude reduction factor $S^*$ is calculated. The unknown scale factor ($B_u$) is then obtained at the value of the characteristic $\sigma^*$. The coordination number follows from $B_u$ and $S^*$ as shown. The BFBT Debye-Waller factors are indicated by $x$. The figure is taken from Teo et al.\textsuperscript{72}
Measurement of Electrical Conductivity

For the electrical measurements, a dilatometer (Netzsch, model 6.801) and a furnace (Netzsch, model 402ET) were specially modified to measure dc electrical conductivity from 100 K to 700 K. The electrical measurement and data analysis were performed by using a data acquisition/controller (Hewlett Packard, model 3852A) and a computer (Hewlett Packard, series 9000, model 310). The measurements were controlled by a program written in BASIC (Hewlett Packard, HP Basic, version 4.0), compiled by a BASIC compiler (IEM, BASIC Compiler, Binary Form). For each recorded data point the program took the average of 10 readings. Typically, one set of data consisted of applied current, voltage drop across the specimen, thermoelectric voltage, thermal expansion of specimen, and temperature.

As a current source, a digital-to-analog converter (Hewlett Packard, model 44727C) was used. The converter (DAC) was operated in the 0–20 mA range at 2.5 μA resolution (voltage compliance < 12 V). As a voltmeter, an analog-to-digital converter (Hewlett Packard, model 44701A; input resistance > 10⁹ Ω) was used. The voltmeter was configured to the 6½ digit mode so as to achieve 10 nV resolution at the 30 mV range and 10 μV resolution at the 30 V range. At this resolution, however, it took approximately 80 seconds to complete a set of measurements, because the voltmeter takes up approximately 267 milliseconds (16 power line cycles) per reading for signal integration. This forced the measurement to carry approximately ±(dT/dt × 80 seconds) of temperature uncertainty, where dT/dt is the time rate of temperature change. The temperature was recorded by measuring the voltage of thermocouple output and converting the voltage into temperature. The conversion was based on polynomial expressions written for various types of thermocouples. The room temperature was compensated by a 5 kΩ thermistor built-in to a relay multiplexer (Hewlett Packard, model 44708A). A 5.306 Ω precision resistor (temperature coefficient < 50 ppm/°C) was used as
a reference resistor for 4-point dc electrical conductivity measurement.

Specimens for dc electrical conductivity measurements were prepared by vacuum hot pressing with the method described earlier. After hot pressing, the surface of the hot-pressed pellet was ground off using a diamond impregnated grinding wheel (Buehler, 70 micron) without lubricant in order to remove graphite residue. The pellet was dry-cut to a size, typically 1 mm thick, 4 mm wide, and 25 mm long, using a diamond impregnated wafering blade (Buehler, 4 inch diameter, high concentration), and a pair of notches were made at approximately 3 mm away from both end of the long dimension. The potential probes were attached to the specimen by winding platinum wire (Johnson Matthey, thermocouple grade, 0.005 inch diameter) twice around the specimen at each notch. Dimensions of the specimen were measured six times, and the average values were used. It is thought that the source of the largest error would be from the distance of the two potential probes, but no statistical treatment was made to estimate the standard deviation.

The dc electrical measurement was done with respect to temperature by using the 4-point method with current reversal technique. In the 4-point method a constant current is applied, and the voltage drop across the specimen is measured. Unlike the 2-point resistance measurement the 4-point method virtually eliminates the effect of a rectifying junction, if one exists. The current reversal technique eliminates the thermoelectric effect, which is generated by a temperature gradient between junctions formed by dissimilar materials. Except for a special purpose, such as verification of ohmic behavior, the default current was set to 2 mA. The method and formula are shown in Figure 8. The temperature of the specimen was measured by using a type-E thermocouple. The heating and cooling rates were 2 K per minute. The electrical conductivity measurements were performed approximately from 100 to 700 K in a purified argon (Air Product, Ultra-Pure Carrier
\[ \sigma = \frac{l}{A}(2I/|V(+I) - V(-I)|) \]

\( \sigma \) : DC electrical conductivity, S cm\(^{-1}\).
I : Current, A.
V : Voltage drop across specimen, V.
l : Distance between two voltage probes, cm.
A : Cross-sectional area of specimen, cm\(^2\)

Figure 8. Four-point current reversal technique used in DC electrical conductivity measurement.
grade) atmosphere. The flow rate was 200 sccm, and the \( \text{P}_{\text{O}_2} \) of the gas was typically \( 10^{-20} \) atm. Fused silica fixtures were used for the measurement.
III. EXPERIMENTAL RESULTS

General Characterization

As shown in Figure 9, a densification of 98% or greater was achieved by hot pressing, but Nb$_{0.32}$Ti$_{0.68}$O$_2$ had approximately 95% of theoretical density. A microscopic examination by SEM (Cambridge Scanning System, model CamScan, series 4) showed that the Nb$_{0.32}$Ti$_{0.68}$O$_2$ contained the highest amount of intergranular microcracks. There was very little difference in powder morphology between Nb$_{0.32}$Ti$_{0.68}$O$_2$ and the others. The grain sizes of hot pressed specimens were all in 8–10 μm range. The formation of microcracks is generally inevitable in polycrystalline materials with large anisotropy because anisotropic thermal expansion along the a- and c-axes within each grain results in an uneven stress on grain boundaries. However, it is not clear why the Nb$_{0.32}$Ti$_{0.68}$O$_2$ shows a lower densification than the others even with the same preparation and consolidation conditions.

The XRD analysis showed that hot pressed solid solutions were of single phase and that the lattice parameters increased with increasing NbO$_2$ concentration. The results are presented in Figure 10. The TiO$_2$ and solid solutions (X<0.8 in Nb$_x$Ti$_{1-x}$O$_2$) have a basic rutile structure, whereas the Nb$_{0.9}$Ti$_{0.1}$O$_2$ and the NbO$_2$ have a deformed rutile structure. The NbO$_2$ and the Nb$_{0.9}$Ti$_{0.1}$O$_2$ showed a series of reflections resulting from the superstructure. These observations of superlattice reflections are in good agreement with those reported by Sakata and Terao. Within the limit of resolution, the lattice parameters determined by XRD are also in good agreement with those determined by TOF neutron diffraction in the present work.
Figure 9. Variation of density in hot pressed Nb$_x$Ti$_{1-x}$O$_2$ solid solutions.
Figure 10. Variation of lattice parameters in $\text{Nb}_x\text{Ti}_{1-x}\text{O}_2$ solid solutions measured by x-ray diffraction technique: (a) Variation of $a$-axis in $\text{Nb}_x\text{Ti}_{1-x}\text{O}_2$ solid solutions. The solid line is drawn by least square fit; (b) Variation of $c$-axis in $\text{Nb}_x\text{Ti}_{1-x}\text{O}_2$ solid solutions. The solid line is drawn to serve as a guide for eyes.
The variation of oxygen content is presented in Figure 11. Although some deviations in oxygen content are noticed at 50 and 90 a/o of Nb, these results suggest that the solid solutions and NbO₂ are superstoichiometric. Only the TiO₂ shows substoichiometric oxygen content. In Figure 11 it can be noticed that there exists a solid solution for which the composition crosses the stoichiometry line (X=2.0) between 0-10 a/o Nb. Generally, an increasing oxygen content with increasing Nb concentration is observed.

**Structural Analysis by Neutron Diffraction**

Figure 12 presents the results of the lattice parameter measurements done by the TOF neutron diffraction technique. The a-parameter shows a linear increase with increasing Nb concentration, whereas the c-parameter deviates very much from linearity especially when the Nb concentration is greater than 32 a/o. The initial linear increase seems to level off starting at 32 a/o of Nb. This result agrees well with that by Rüdorff and Luginsland except that the a-parameters of Nb₀.₅Ti₀.₅O₂ and Nb₀.₆Ti₀.₄O₂ show small deviations from the linearity. The c-parameters of the two compositions also show a small mismatch with other works. The variations of the position parameter (u,u,0) of oxygen, the cation-anion (M-O) bond lengths, and the cation-anion-cation (M-O-M) bond angle are shown in Figures 13, 14, and 15, respectively. Small deviations from linearity can be noticed in Figures 13, 14, and 15. Figure 16 presents the results of structural refinement done for occupancy factors of octahedral and tetrahedral interstitial sites at (0.5,0,0.5) and (0.135,0.135,0.5), respectively.

**X-ray Absorption Near Edge Structure**

Figure 17 shows the normalized Nb K-edge XANES of NbO₂. Also in Figure 17 the first and the second derivatives of XANES spectrum are shown, and various XANES features are labeled. The XANES spectra, the first and the second
Figure 11. Variation of oxygen content, 2+Y, in Nb$_x$Ti$_{1-x}$O$_{2+y}$ solid solutions determined by thermogravimetric analysis.
Figure 12. Variation of lattice parameters in Nb$_x$Ti$_{1-x}$O$_2$ solid solutions determined by least square refinement of time-of-flight neutron diffraction data: (a) Variation of $a$-axis in Nb$_x$Ti$_{1-x}$O$_2$ solid solutions. The solid line is drawn by least square fit; (b) Variation of $c$-axis in Nb$_x$Ti$_{1-x}$O$_2$ solid solutions. The solid line is drawn to serve as a guide for eyes.
Figure 13. Variation of position parameter of oxygen at (u,u,0) in Nb$_x$Ti$_{1-x}$O$_2$ solid solutions determined by Rietveld analysis of neutron diffraction data. The solid line is drawn by least square fit.
Figure 14. Variation of metal-to-oxygen distances ($r_{M-O}$) in $\text{Nb}_x \text{Ti}_{1-x} \text{O}_2$ solid solutions calculated from the result of Rietveld analysis. The solid lines are drawn by least square fit.
Figure 15. Variation of metal-oxygen-metal bond angle in Nb$_x$Ti$_{1-x}$O$_2$ solid solutions calculated from the result of Rietveld analysis. The solid line is drawn by least square fit.
Figure 16. Variation of occupancies of octahedral and tetrahedral interstitial sites in \( \text{Nb}_x \text{Ti}_{1-x} \text{O}_2 \) solid solutions determined by Rietveld analysis of neutron diffraction data.
Figure 17. Normalized Nb K-edge XANES, the first and the second derivatives of Nb$_{0.1}$Ti$_{0.9}$O$_2$ solid solutions. The preedge shoulder (PESh), the edge inflection point (IP), the first edge peak (EPI), and the second edge peak (EP2) are shown.
derivatives of the other solid solutions are given in Appendix. Each spectrum is characterized by three features: (1) a weak preedge shoulder at approximately 18.982 eV, which is due to an electronic transition from the 1s core to the empty 4d valence state of Nb ions; (2) an unresolved peak (more like an inflection point) in the midst of the absorption edge at approximately 18.996 eV, which is due to a transition from 1s to 4p; and (3) two strong edge peaks at approximately 19.005 and 19.015 eV, which are due to multiple scattering resonances of photoelectron by neighboring atoms. The close similarity of the XANES spectra suggests tentatively that the site symmetry of Nb ions are very much the same for all compositions. Also, the fact that the position of the inflection point stays almost constant suggests that the formal valence of Nb ions are the same for all compounds. On the other hand, the variation of the preedge shoulder, i.e., increasing position in energy scale with decreasing Nb concentration, implies that the concentration of Nb ions with valence higher than 4+ are increasing with decreasing Nb concentration. As reported by Wong, an increase of 1-2 eV in preedge position is expected for an increase of valence by 1. Thus, it appears that the ratio of Nb$^{5+}$ to Nb$^{4+}$ is higher in low Nb concentrations than in high Nb concentrations. The variations of the XANES features in terms of energy are shown in Figure 19.

**Extended X-ray Absorption Fine Structure**

The normalized and background-subtracted Nb K-edge EXAFS ($k^3 \chi(k)$ vs. $k$) and the Fourier transforms of the EXAFS of NbO$_2$ are presented in Figure 19 and Figure 20, respectively. Those for the other compositions are given in Appendix. The oscillations in the EXAFS are due to backscattering of all ions about the central Nb ions, but generally those oscillations in the range from 0 to 5 Å$^{-1}$ contribute to the position, shape, and intensity of the principal peak at approximately 1.4 Å in the PRDF. Since the Fourier transform does not account for
Figure 18. Variations of Nb K-edge XANES features of Nb$_x$Ti$_{1-x}$O$_2$ solid solutions.
Figure 19. Background-subtracted, $k^3$-weighted Nb K-edge EXAFS of Nb$_{0.1}$Ti$_{0.9}$O$_2$. 

Figure 20. Fourier transform of the Nb K-edge EXAFS of NbO$_2$. 
phase shift, each peak in the PRDF represents individual coordination shells in pseudo radial distance space, but not in the real distance space.

The principal peak in PRDF of NbO$_2$ (the model compound) is due to backscattering from the nearest neighbor about Nb, and thus the peak is assigned to oxygen. The other peaks in the range roughly between 2 to 4 Å in the PRDF are due to the backscattering from the second and higher coordination shells, but it can be readily understood from the crystal structure of rutile that the second peak in PRDF has to be due to backscattering from niobium. The third and higher coordination peaks can be assigned to either oxygen or niobium. However, since the theoretical backscattering amplitudes shown in Figure 5 indicate that the backscattering amplitude of oxygen is very much smaller than that of niobium, all peaks in the range from 2 to 4 Å are assigned also to niobium.

In the PRDF of solid solutions the intensities of Nb peaks gradually decrease with decreasing Nb concentration. Also, as Nb concentration decreases, new peaks due to backscattering from titanium start to evolve. However, the overall intensities of the metal peaks decrease gradually, but start to increase again through a minimum near the Nb concentration of 70 a/o. This is because of the difference in backscatterer phase shift, as shown in Figure 5, which results in a destructive interference of backscattering amplitudes between niobium and titanium atoms.

The inverse Fourier transform of the filtered oxygen peak (i.e., Fourier filtered $k^3 \chi(k)$ vs. $k$) and the BFBT curves for Nb$_{0.1}$Ti$_{0.9}$O$_2$ are presented in Figure 21. Those for other compositions are given in Appendix. In Figure 22 the parameters obtained by BFBT are displayed in terms of composition. The increasing trends of $r_{\text{Nb-O}}$ and $\sigma_{\text{DW}}$ with increasing Nb concentration are in agreement with other diffraction works.$^{31,36,37}$ However, there is a noticeable variation in $\Delta E_0$, approximately 3 eV, which affects directly the $r_{\text{Nb-O}}$. According
Figure 21. Fourier filtered Nb K-edge EXAFS of Nb$_{0.1}$Ti$_{0.9}$O$_2$ solid solutions. The dashed line is the best fit based on theory.
Figure 22. Variations of parameters (scale factor, Debye-Waller factor, interatomic distance, and energy shift) obtained by BFBT curve fitting on Fourier filtered oxygen shell.
(a) Variation of scale factor (B) obtained by BFBT curve fitting on Fourier filtered oxygen shell. (b) Variation of Debye-Waller ($\sigma_{DW}$) factor obtained by BFBT curve fitting on Fourier filtered oxygen shell.
(c) Variation of interatomic distance ($r_{\text{Nb-O}}$) obtained by BFBT curve fitting on Fourier filtered oxygen shell. (d) Variation of energy shift ($\Delta E_0$) obtained by BFBT curve fitting on Fourier filtered oxygen shell.
to Antonio, a change in $\Delta E_0$ by 1-3 eV causes a corresponding change in the $r$ by approximately 0.01 Å.

The parameter correlations for interatomic distance ($\Delta E_0$ vs. $\Delta r_{\text{Nb-O}}$) and scale factor (B vs. $\sigma_{\text{DW}}$) are plotted in Figure 23 and Figure 24, respectively. According to Antonio, the criteria for a good model are: (1) the slopes in $\Delta E_0$ vs. $\Delta r_{\text{Nb-O}}$ plots must be very similar, and the resulting correction in distance $\Delta r$ for the unknowns must be within ±0.1 Å from the best fit value; and (2) the best fit $\sigma_{\text{DW}}$ for the model and the unknowns must be similar. Thus, it appears that the NbO$_2$ was a good choice as a model in the present study.

The interatomic distances ($r_{\text{Nb-O}}$) corrected by FABM based on the $\Delta E_0$ vs. $\Delta r_{\text{Nb-O}}$ correlations are presented in Figure 25. The $r_{\text{Nb-O}}$ increases with Nb concentration in a linear fashion, as seen in the variation of $a$-parameter in Figure 12. In Figure 25 the average metal-to-oxygen distances ($r_{\text{M-O, Avg}}$) calculated from the neutron diffraction data are also plotted. The $r_{\text{M-O, Avg}}$ was calculated as follows:

$$r_{\text{M-O, Avg}} = \frac{2r_{\text{M-O, (110)}} + 4r_{\text{M-O, Other}}}{6},$$

(10)

where $r_{\text{M-O, (110)}}$ is the metal-to-oxygen distance on the (110) plane, i.e., the M-O distance from the body-centered metal to the oxygen at the vertex of octahedra, and $r_{\text{M-O, Other}}$ that on the plane perpendicular to (110), i.e., the M-O distance on the base of octahedra. The $r_{\text{Nb-O}}$ obtained by FABM shows an agreement with the average $r_{\text{M-O}}$ calculated from neutron diffraction data.

The coordination numbers obtained by FABM are shown in Figure 26. The variation of coordination number shows a decreasing trend from 6 for NbO$_2$ (the model compound) to 5 for Nb$_{0.1}$Ti$_{0.9}$O$_2$ with decreasing Nb concentration. This implies that some fraction of Nb enters into the tetrahedrally coordinated lattice.
Figure 23. FABM interatomic distance correlation curves for $\text{Nb}_x\text{Ti}_{1-x}\text{O}_2$ solid solutions.
Figure 24. FABM coordination number correlation curves for Nb$_X$Ti$_{1-X}$O$_2$ solid solutions.
Figure 25. Variation of Nb-O distance ($r_{\text{Nb-O}}$) in Nb$_x$Ti$_{1-x}$O$_2$ solid solutions adjusted by FABM technique. For comparison, the variation of interatomic distance ($r_{\text{M-O, avg}}$) obtained by neutron diffraction experiment is also shown.
Figure 26. Variation of coordination number obtained by FABM in Nb$_x$Ti$_{1-x}$O$_2$ solid solutions. The solid line (least square fit) serves as a guide for eyes.
positions as well as into the octahedrally coordinated regular cation sites. It is noticed that the result shows a scattering of data points throughout the range of composition. Surprisingly, however, the pattern of variation in coordination number follows very closely to that in actual thickness normalized against the ideal thickness of the specimen as shown in Figure 27. Several reports have mentioned the thickness effect in XAS experiment in transmission mode,\textsuperscript{73, 77-81} but no numerical technique for post-treatment has been available. This is probably because of the difficulty in preparing a thin specimen, whose thickness must be well characterized and have a small variance, without any pinholes or cracks.

Figure 28 presents the variation of the first pseudo radial Nb-Nb distance with respect to composition. Although the Fourier filtering was not performed, the positional variation of the second peak in the PRDF (due to backscattering from nearest Nb) describes roughly how the Nb-Nb distance would vary in the real radial space.

**DC Electrical Conductivity**

The raw data of the dc electrical conductivity measurements are given in Appendix. The raw data show that some hysteresis in electrical conductivity exists during the heating and cooling cycle. Generally, the hysteresis is related to the order of transition, but in the present case it is believed to be the result of anisotropy of thermal expansion that often results in intergranular microcracks.\textsuperscript{75} In Figure 29 the dc electrical conductivity at 305 K is shown as a function of Nb concentration. The conductivity showed a wide variation with composition: approximately, from $4.4 \ \Omega^{-1} \text{cm}^{-1}$ for TiO$_2$ to $2.8 \times 10^{-3} \ \Omega^{-1} \text{cm}^{-1}$ for NbO$_2$ with a conductivity peak of $53 \ \Omega^{-1} \text{cm}^{-1}$ at Nb$_{0.1}$Ti$_{0.9}$O$_2$. As seen in Figure 11, the TGA result indicates that the oxygen content becomes substoichiometric at some composition below 10 a/o Nb. However, the fluctuations in oxygen content near 50 and 90 a/o do not seem to affect the electrical conductivity. The activation energy
Figure 27. Normalized thickness (actual thickness divided by ideal thickness) vs. Nb concentration.
Figure 28. Variation of Nb-Nb distance in pseudo radial distribution function of Nb\textsubscript{x}Ti\textsubscript{1-x}O\textsubscript{2} solid solutions. The solid line is drawn to serve as a guide for eyes.
Figure 29. Variation of DC electrical conductivity with respect to composition. Data points are taken at 305 K: (a) Variation of DC electrical conductivity displayed on linear scale; (b) Variation of DC electrical conductivity displayed on logarithmic scale.
for conduction was calculated by the following relation:

$$\sigma = \sigma_0 \exp(-E_a/kT),$$

(11)

where the activation energy for conduction is given by $E_a = E_C - E_F$. Figure 30 shows the variation of $E_a$ versus composition. The activation energy increases almost linearly from TiO$_2$ to Nb$_{0.9}$Ti$_{0.1}$O$_2$, and then sharply to NbO$_2$. 
Figure 30. Variation of activation energy for conduction with respect to Nb concentration.
IV. DISCUSSION

The main objective of the present research is to investigate the defect structure and the dc electrical conductivity of TiO$_2$-NbO$_2$ solid solution by using various experimental techniques. In the present research, five different experiments and analyses have been conducted: structural analysis by neutron diffraction, identification of cation valence by XANES analysis, determination of coordination number by EXAFS analysis, determination of nonstoichiometry by thermogravimetric analysis, and measurement of dc electrical conductivity by 4-point current reversal technique. It is the objective of this chapter to analyze the results and to discuss the problems for a better understanding of the defect structure and the dc electrical conductivity of TiO$_2$-NbO$_2$ solid solutions.

In Figure 12, the increase of the $a$- and $c$-parameters with increasing Nb concentration is shown, and the results are in good agreement with other works.$^{68}$ It is observed that the extent of variation in the $c$-parameter is much smaller than that in the $a$-parameter. From 10 to 40 a/o of Nb concentration, for example, the $c$-parameter increases by 0.0218 Å, while the $a$-parameter increases by as much as 0.0762 Å. This suggests that the cation-cation interaction becomes stronger along the $c$-axis with Nb concentration, and that the interaction suppresses the elongation of $c$-axis. As a result, the suppression of the elongation of the $c$-parameter by cation-cation bond formation is reflected by the other crystallographic parameters: the position parameter (u,u,0) of oxygen shown in Figure 13, cation-anion (M-O) bond lengths shown in Figure 14, and the cation-anion-cation (M-O-M) bond angle shown in Figure 15.

As shown in Figure 14, with increasing Nb concentration, the M-OOther
distance increases linearly, whereas the $M-O_{(110)}$ distance seems to remain constant. At approximately 28 a/o of Nb concentration, the $M-O_{\text{Other}}$ distance becomes equal to $M-O_{(110)}$ distance. Although the $M-O_{(110)}$ distance appears to be essentially constant, it is interesting to note that there exists a small variation in $M-O_{(110)}$ distance. The trend seems to have a close similarity to the variation in the $M-O-M$ bond angle shown in Figure 15 and the oxygen position parameter shown in Figure 13. Thus, it is thought that the increase in the $M-O_{\text{Other}}$ distance is absorbed by a decrease in the $M-O-M$ bond angle shown in Figure 15, and that the net effect is the suppression of the elongation of c-axis. Other evidence for the cation-cation bond formation can be found from the softening of the rate of increase of the c-parameter. In Figure 12 the increase in the c-parameter starts to level off near $\text{Nb}_{0.32}\text{Ti}_{0.68}\text{O}_2$ as the Nb concentration increases. Sakata attributed this to the preferential formation of Nb-Nb bonds along the c-axis, and he noticed that the deviation from a linear increase begins near an Nb concentration of 30 a/o or less.

As shown in Figure 16, from 10 to 40 a/o of Nb concentration, the Nb ions occupy the tetrahedral interstitial sites as well as the regular cation sites, but the population of tetrahedral interstitial Nb ion decreases with increasing Nb content and eventually vanishes at 40 a/o. The Ti ions start to occupy octahedral interstitial sites at 32 a/o of Nb concentration, and the occupancy of octahedral sites by Ti ions peaks at an Nb concentration between 50 and 60 a/o. As a whole, the following is observed: with increasing Nb concentration the Nb ions, which took the tetrahedral interstitial sites at lower Nb concentrations, tend to occupy the regular cation sites by driving host Ti ions into tetrahedral and octahedral interstitial positions. It seems that these migrations of cations bring some change in defect structure, and the change also involves modification of cation valences.

From the chemistry of $\text{TiO}_2$ and $\text{NbO}_2$, the valence of Ti and Nb is 4+ if the
two form a perfect substitutional solid solution, $\text{Nb}_x\text{Ti}_{1-x}\text{O}_2$. As discussed earlier, however, the XANES data indicate that some Nb ions have valence $5^+$ at low Nb concentration, but it is not clear how $\text{Nb}^{5+}$ ions are distributed between tetrahedral interstitial and regular cation sites. When the interstitial occupancy is normalized with respect to cation concentration (i.e., $X$ in $\text{Nb}_x\text{Ti}_{1-x}\text{O}_2$) as shown in Figure 31, it is evident that a large fraction of Nb ions indeed occupy the interstitial sites at low Nb concentration.

If the Nb ions in the regular cation sites interact with each other to form Nb-Nb pairs, which would have a strong covalent nature of bonding, it is expected that there would be a significant change in electrical conductivity. That is, when the Nb concentration is low, the Nb ions are dispersed homogeneously in the TiO$_2$ matrix, and naturally the probability is low for Nb ions to see each other to form a pair. However, as the Nb concentration increases, the distance between Nb ions becomes shorter, and the Nb ions start interacting with each other to form a bond. In order to form a bond, the unpaired 4d-electrons, which would have been free in the d-band, have to be reclaimed by the Nb ions and have to be localized between two Nb ions. This probably is one of the explanations for the preferential dimerization along the c-axis as postulated by Sakata$^{36,60}$.

As shown in Figure 29(a), the electrical conductivity at room temperature increases sharply from 0 to 10 a/o of Nb concentration, but the conductivity decreases with a further increase in Nb concentration. The initial sharp increase in electrical conductivity is probably due to an increase in concentration of Nb$^{4+}$ ions that have unpaired 4d-electrons and act as electron donors. Thus, in line with the results of neutron diffraction, it is tempting to suggest that the Nb ions entering into the tetrahedral interstitial sites become ionized to Nb$^{5+}$ and make extra charge carriers available for the electrical conduction, but it is unfortunate that the present results of XANES can not be treated quantitatively to identify the
Figure 31. Variation of occupancies of octahedral and tetrahedral interstitial sites normalized with respect to \( X \) for Nb and to \( 1-X \) for Ti in \( \text{Nb}_X\text{Ti}_{1-X}\text{O}_2 \) solid solutions determined by Rietveld analysis of neutron diffraction data.
\( \text{Nb}^{5+}/\text{Nb}^{4+} \) ratio because of the lack of site specificity and the uncertainty due to thickness effects.

The decrease of electrical conductivity above 10 a/o of Nb concentration implies that there has to be a mechanism that lowers the carrier concentration, providing that there is no drastic change in carrier mobility with varying Nb concentration. Thus, the peak in electrical conductivity is thought to be an indication of an onset of dimerization of Nb ions, where the pairing of Nb ions along the \( c \)-axis begins. Therefore, the variation of electrical conductivity with Nb concentration can be described as a competition between the following two processes: (1) the ionization of Nb ions, which sets electrons free; and (2) the formation of Nb-Nb pairs, which confines electrons in Nb-Nb pairs and limits them from participating in the electrical conduction. As a supporting evidence, a decreasing Nb concentration in the tetrahedral interstitial sites is noticed in Figure 31. This suggests that when a small amount of Nb ion is added into TiO\(_2\), the Nb ions enter into the tetrahedral interstitial sites as well as into the regular cation sites; but, as the Nb concentration increases, the Nb ions enter preferentially into the regular cation sites to form Nb-Nb pairs. Therefore, it may be tempting to suggest that the composition for the onset of Nb-Nb pair formation imposes a limit in the solubility of Nb\(^{5+}\) in TiO\(_2\). Eror\(^{57}\) reported the solubility limit of approximately 8 a/o of Nb\(^{5+}\) ions in TiO\(_2\), and Valigi et al.\(^{58}\) claimed approximately 6 a/o.

The decrease of electrical conductivity above the Nb concentration of 10 a/o in Figure 29(a) is in good agreement with the results of Sakata et al.\(^{82}\) They presented the results in a logarithmic scale and attributed the slow logarithmic decrease of electrical conductivity to the formation of Nb-Nb pairs. When the present results shown in Figure 29(a) are reviewed in a logarithmic scale as shown in Figure 29(b), the slow logarithmic decrease in electrical conductivity can also
be noticed from 10 to 70 a/o of Nb concentration. Although it is not clear if there truly is an exponential dependence of electrical conductivity on Nb concentration, the visualization in the logarithmic scale certainly helps viewing the variation in the Nb-rich end.

In Figure 30 the activation energy for conduction increases slowly from TiO₂ (Eₐ≈0.05 eV) to 80 a/o (Eₐ≈0.25 eV) of Nb concentration, and from there it shows a somewhat steeper increase toward NbO₂₄ (Eₐ≈0.4 eV). The activation energy varies almost linearly from TiO₂ to Nb₀.₈Ti₀.₂O₂. The activation energy, approximately 0.4 eV, of NbO₂₄ seems very close to the thermal gap, 0.5 eV, reported by Poulmellic and Marucco. If the activation energy estimated in the present study corresponds to the thermal gap, which is due to the niobium coupling, i.e., bond formation, then the initial increase in activation energy is probably due to a transition from a donor state to a coupling state.

In the intermediate Nb concentrations, it appears that all the niobium ions are in a bound state, and that all the electronic activities are due to interstitial titanium ions. This can be understood from the result of the least square analysis of the neutron diffraction data shown in Figure 16 and Figure 31, where the interstitial concentration of Ti is high. Thus, an interstitial Ti state (Tiᵢ*** or Tiᵢ****: the charge states of the interstitial Ti ions are not discernable in the present research) can be suggested as a type of defect in the range 0.4<X<0.8; but it is evident that interstitial Ti can not be the majority defect because the results of TGA indicate that the solid solutions are all oxygen excess (or metal deficient). Unfortunately, with the results of the present research it is not possible to tell whether there exists any vacancy states (V*ₙ₅b) as claimed by Marucco et al.

In the high Nb concentrations to NbO₂₄, the Nb coupling is strong enough to cause a structural modification. In order to have lower conductivity and to have higher activation energy as seen in Figure 29 and Figure 30, respectively, either
the electrons become less mobile, or the concentration of electrons must decrease. At this stage, according to Figure 16, the Nb ions start appearing into octahedral interstitial positions and coexist with interstitial Ti ions. The valence of the interstitial Nb ion is uncertain at present because of the following reasons: (1) a small fraction of the total Nb ions are at the interstitial position; (2) the resolution of XANES may not be high enough to reliably and quantitatively identify the valence of the Nb at the octahedral interstitial site; and (3) there also exists a high concentration of Ti interstitials (and possibly neutral Nb vacancies as suggested by Marucco et al.55) that makes the interpretation more difficult. Marucco et al.55 suggested that the neutral niobium vacancy ($V_{\text{Nb}}^*$) is the main defect in the Nb-rich side, but their results indicated that the titanium vacancy ($V_{\text{Ti}}^*$) can be created more easily than the niobium vacancies ($V_{\text{Nb}}^*$).

As shown in Figure 18 the position of the edge inflection point remains essentially constant. This means that the formal valence of the Nb ion is 4+ for all solid solutions and NbO$_2$. This is consistent with the way that TiO$_2$ and NbO$_2$ form a continuous solid solution by substitution. In the present result the edge inflection point suffers from the thickness effect. However, no evident shift due to thickness variation is noticed in the preedge shoulder. The reason is that the higher the absorption, the more the feature (e.g., edge inflection point) is subject to the thickness effect. Thus, it is believed that the preedge shoulder contains the information that is the least affected by varying thickness. There is one thing to note about the preedge shoulder: although the transition from 1s to 4d states is strictly dipole forbidden in regular octahedra because of a center of inversion, a preedge feature is noticed as shown in Figure 17. In the present study, however, this transition is possible because of the broken inversion symmetry in the rutile structure, which has a slightly distorted octahedron as seen from the neutron diffraction data. Since the preedge absorption arises from the electronic transition
from 1s to 4d, the positional variation of the preedge shoulder tells more about the change of oxidation state of the Nb ions than that of the edge inflection point does.

In Figure 18 the position of the preedge shoulder decreases with increasing Nb concentration. This positive shift of preedge position can be understood as follows: when an atom loses its outer electron, the attractive potential of the nucleus on the 1s-electron increases, and the repulsive Coulomb interaction between the core and all other electrons decreases. From the chemistry of NbO₂ (the model compound in the present study), one knows that the valence of Nb must be 4+, so the 4d-orbital has only one electron. This means that the Nb ions become more positive and attain Nb⁵⁺ characters with decreasing Nb concentration. Except for the point at 90 a/o of Nb, a smooth increase in preedge position is seen. Also, it is noticed that the way that preedge shoulder position varies has a close similarity to the variation of electrical conductivity shown in Figure 29 and activation energy shown in Figure 30. The positional variation of the preedge shoulder can be accounted for by the apparent increase in valence with decreasing Nb concentration, which is due to the increasing tendency to share the unpaired 4d-electrons with Ti ions. The Ti ions are in interstitial sites according to the analysis of neutron diffraction data shown in Figure 16, and the chemical state is probably Ti⁴⁺ according to Poumellec et al.⁶³ The results seem to agree with Valigi et al.⁵⁸ who suggested the presence of Ti⁴⁺ in TiO₂-NbO₂ solid solution by TGA and EPR experiments, but the range of Nb concentration they studied (0-10 a/o Nb) is not covered in the present study. The present Nb K-edge XANES analysis agrees with the Ti K-edge XANES analysis by Poumellec et al.⁶³ Poumellec et al. suggested an electron exchange between Ti and Nb ions because the energy levels of Ti³⁺ and Nb⁴⁺ are the same.

As shown in Figure 26 the coordination number decreases from NbO₂ (the
model compound) to Nb$_{0.1}$Ti$_{0.9}$O$_2$. However, the coordination number is neither 4 nor 6 at low Nb concentration, implying that some fraction of Nb ions are in tetrahedrally coordinated sites. The variation of coordination number suggests that at low Nb concentration the Nb ions occupy tetrahedral interstitial positions, but with increasing Nb concentration the Nb ions enter into the structure substitutionally and take the octahedrally coordinated regular cation sites. Although further interpretation of the EXAFS result is now limited by badly scattered data points suffering from thickness effects, the present analysis on coordination number by the FABM technique is in general agreement with the neutron diffraction results shown in Figure 16. The reason that the analysis of coordination number suffers from the thickness effect is primarily because the varying thickness affects greatly the amplitude of EXAFS particularly in the transmission measurement. Thus the scale factor (B) obtained by nonlinear least square curve fitting of EXAFS can result in an incorrect value, and the coordination number determined from that incorrect scale factor can be seriously misleading. In the present research, the specimens were prepared based on calculated ideal thicknesses. However, it was realized that the preparation of thin specimens (20–100 µm) with negligible variance was very difficult to achieve. Thus the following procedure is suggested for future experiments: (1) specimens with identical thickness are prepared; and (2) based on the thickness, the gas pressure in the detector is adjusted to obtain an absorption edge jump of unity. Also, the use of krypton gas is suggested because the absorption by krypton is an order of magnitude higher than that by argon, and the use of krypton will improve significantly the data quality at high k.

As shown in Figure 25, the Nb–O distance ($r_{\text{Nb-O}}$) increases linearly with increasing Nb concentration, but it should be pointed out that the $r_{\text{Nb-O}}$ is the average Nb–O distance of $r_{\text{Nb-O, (110)}}$ and $r_{\text{Nb-O, Other}}$. The smooth, continuous
variation of Nb-O distance is taken as evidence that the Nb dissolves into TiO$_2$ homogeneously to form a complete solid solution Nb$_x$Ti$_{1-x}$O$_2$. This also suggests that the crystallographic change from the basic to the deformed rutile structure is not abrupt but continuous. The interatomic distances obtained by neutron diffraction ($r_{M-O}$) and by EXAFS and FABM ($r_{Nb-O}$) are in good agreement as shown in Figure 25.

In the present analysis of EXAFS, the Fourier filtering, curve fitting, and FABM treatment were conducted only on the first coordination shell, i.e., oxygen. However, some extended analysis can be made with good quality data by simply tracing the variation of other peak positions in the PRDF such as that shown in Figure 20. In PRDF the radial distance is not the true distance because phase shift correction is not applied, but it maintains a proportionality for a given coordination shell. In Figure 28 the Nb-Nb pseudo radial distance increases with increasing Nb concentration, but it starts to level off near 32 a/o of Nb. The variation closely simulates the variation of the c-parameter shown in Figure 12(b). In Figure 28 there are no available data points for Nb concentrations lower than 10 a/o, but it is believed that at some point the distance will start to increase rapidly as the Nb concentration approaches to zero. When the Nb concentration increases to a certain value, the second nearest Nb coordination shell forms and starts to backscatter photoelectrons. According to the neutron diffraction results shown in Figure 12, the unit cell expands with increasing Nb concentration. Thus the Nb-Nb distance increases accordingly. This is seen in Figure 28 at low Nb concentration roughly up to 20 a/o. However, with a further increase in Nb concentration, the Nb ions start to interact with each other to form a pair. The smooth decrease in the rate that the Nb-Nb pseudo radial distance increases is an indication that Nb ions are forming pairs. In forming pairs, no abrupt change in distance is expected, and thus the effect of pair formation is gradually reflected
by the change in distance because the distance is the average value of all Nb ions. Therefore, it is thought that the pair formation is initiated at an Nb concentration below 20 a/o, which is lower than the 30 a/o reported by Sakata.\textsuperscript{60} Also, it is suggested that the Nb concentration for the initiation of pair formation may be as low as 6-8 a/o of Nb concentration. The effect of pair formation can be noticed in the variation of the lattice parameters as shown in Figure 12, and the following is observed: (1) at low Nb concentrations the lattice parameters expand because the Nb ions with larger ionic radius substitute for Ti ions; and (2) with increasing Nb concentration the rate of growth of the c-parameter slows down, while that of the a-parameter remains constant. Thus, it appears that the strong Nb-Nb interaction along the c-axis suppresses the elongation of the c-parameter and allows the unit cell to expand more freely along the a-axis. This is the first observation of Nb-Nb interaction in TiO\textsubscript{2}-NbO\textsubscript{2} solid solutions with basic rutile structure and is direct evidence that the Nb-Nb interaction is responsible for the way that the lattice parameter varies as shown in Figure 12. This verifies the postulate of Sakata.\textsuperscript{36, 60}
V. CONCLUSION

The formation of Nb-Nb pair bonds is observed. The pair formation seems to start at Nb concentration as low as 6-8 a/o. The initial expansion of cell parameters is due to the introduction of Nb ions that have larger ionic radius than Ti ions. With increasing Nb concentration the expansion of c-parameter is suppressed, while the a-parameter increases linearly. The suppression of the expansion of the c-parameter with increasing Nb concentration is attributed to the formation of Nb-Nb pairs, which restrains the unit cell from expanding along the c-axis and allows it to grow preferentially along the a-axis. The effect of Nb-Nb pair formation is also noticed in the electrical conductivity measurement. The electrical conductivity shows a maximum at 10 a/o of Nb concentration and decreases with increasing Nb concentration. The decrease in conductivity with increasing Nb concentration is also attributed to the Nb-Nb pair formation. The coordination number of the Nb ions seems to decrease with decreasing Nb concentration, implying that Nb ions occupy tetrahedral interstitial sites as well as regular cation sites at low Nb concentration. With increasing Nb concentration, the Nb population in the tetrahedral interstitial sites decreases and disappears at 32 a/o of Nb concentration, while the populations of Ti ions in octahedral and tetrahedral interstitial sites increase. The effective valence of Nb ions increases from 4+ to 5+ with decreasing Nb concentration, but the formal valence of Nb ions remains at 4+. This is probably an indication of the 4d-electron in Nb$^{4+}$ being donated to, or shared with, Ti$^{4+}$ with decreasing Nb concentration. The consequence is the creation of Ti ions with an apparent charge of 3+ and Nb ions with that of 5+.
Stacked plot of normalized Nb K-edge XANES. The numbers on each spectrum are 1 for $\text{Nb}_{0.1}\text{Ti}_{0.9}\text{O}_2$, 2 for $\text{Nb}_{0.2}\text{Ti}_{0.8}\text{O}_2$, 3 for $\text{Nb}_{0.3}\text{Ti}_{0.68}\text{O}_2$, 4 for $\text{Nb}_{0.4}\text{Ti}_{0.6}\text{O}_2$, 5 for $\text{Nb}_{0.5}\text{Ti}_{0.5}\text{O}_2$, 6 for $\text{Nb}_{0.6}\text{Ti}_{0.4}\text{O}_2$, 7 for $\text{Nb}_{0.7}\text{Ti}_{0.3}\text{O}_2$, 8 for $\text{Nb}_{0.8}\text{Ti}_{0.2}\text{O}_2$, 9 for $\text{Nb}_{0.9}\text{Ti}_{0.1}\text{O}_2$, and 10 for $\text{NbO}_2$. 
The raw data, the first and the second derivatives of normalized Nb K-edge XANES of Nb$_{0.1}$Ti$_{0.9}$O$_2$. 
The raw data, the first and the second derivatives of normalized Nb K-edge XANES of Nb$_{0.2}$Ti$_{0.8}$O$_2$. 
The raw data, the first and the second derivatives of normalized Nb K-edge XANES of Nb$_{0.32}$Ti$_{0.68}$O$_2$. 
The raw data, the first and the second derivatives of normalized Nb K-edge XANES of Nb_{0.4}Ti_{0.6}O_{2}.
The raw data, the first and the second derivatives of normalized Nb K-edge XANES of Nb$_{0.5}$Ti$_{0.5}$O$_2$. 
The raw data, the first and the second derivatives of normalized Nb K-edge XANES of Nb$_{0.6}$Ti$_{0.4}$O$_2$. 
The raw data, the first and the second derivatives of normalized Nb K-edge XANES of Nb$_{0.7}$Ti$_{0.3}$O$_3$. 
The raw data, the first and the second derivatives of normalized Nb K-edge XANES of Nb$_{0.8}$Ti$_{0.2}$O$_{2}$.
The raw data, the first and the second derivatives of normalized Nb K-edge XANES of Nb$_{0.9}$Ti$_{0.1}$O$_2$. 
The raw data, the first and the second derivatives of normalized Nb K-edge XANES of NbO$_2$. 
Stacked plot of background-subtracted, $k^3$-weighted Nb K-edge EXAFS of Nb$_{2}$Ti$_{1-x}$O$_{2}$ solid solutions. The numbers on each spectrum are 1 for Nb$_{0.1}$Ti$_{0.9}$O$_{2}$, 2 for Nb$_{0.2}$Ti$_{0.8}$O$_{2}$, 3 for Nb$_{0.3}$Ti$_{0.7}$O$_{2}$, 4 for Nb$_{0.4}$Ti$_{0.6}$O$_{2}$, 5 for Nb$_{0.5}$Ti$_{0.5}$O$_{2}$, 6 for Nb$_{0.6}$Ti$_{0.4}$O$_{2}$, 7 for Nb$_{0.7}$Ti$_{0.3}$O$_{2}$, 8 for Nb$_{0.8}$Ti$_{0.2}$O$_{2}$, 9 for Nb$_{0.9}$Ti$_{0.1}$O$_{2}$, and 10 for NbO$_{2}$. 

Stacked plot of the Fourier transforms of the Nb K-edge EXAFS. The numbers on each spectrum are 1 for Nb$_{0.1}$Ti$_{0.9}$O$_2$, 2 for Nb$_{0.2}$Ti$_{0.8}$O$_2$, 3 for Nb$_{0.3}$Ti$_{0.6}$O$_2$, 4 for Nb$_{0.4}$Ti$_{0.5}$O$_2$, 5 for Nb$_{0.5}$Ti$_{0.5}$O$_2$, 6 for Nb$_{0.6}$Ti$_{0.4}$O$_2$, 7 for Nb$_{0.7}$Ti$_{0.3}$O$_2$, 8 for Nb$_{0.8}$Ti$_{0.2}$O$_2$, 9 for Nb$_{0.9}$Ti$_{0.1}$O$_2$, and 10 for NbO$_2$. 

$r'$ in Angstroms
Result of curve fitting by BFBT (shown in dashed line) on $\text{Nb}_{0.3}\text{Ti}_{0.7}\text{O}_2$. The dashed line shown in the PRDF is the Hanning window applied to filter out the oxygen shell.
Result of curve fitting by BFBT (shown in dashed line) on Nb$_{0.2}$Ti$_{0.8}$O$_2$. The dashed line shown in the PRDF is the Hanning window applied to filter out the oxygen shell.
Result of curve fitting by BFBT (shown in dashed line) on Nb$_{0.32}$Ti$_{0.68}$O$_2$. The dashed line shown in the PRDF is the Hanning window applied to filter out the oxygen shell.
Result of curve fitting by BFBT (shown in dashed line) on Nb$_{0.4}$Ti$_{0.6}$O$_2$. The dashed line shown in the PRDF is the Hanning window applied to filter out the oxygen shell.
Result of curve fitting by BFBT (shown in dashed line) on Nb$_{0.5}$Ti$_{0.5}$O$_3$. The dashed line shown in the PRDF is the Hanning window applied to filter out the oxygen shell.
Result of curve fitting by BFBT (shown in dashed line) on Nb$_{0.5}$Ti$_{0.4}$O$_3$. The dashed line shown in the PRDF is the Hanning window applied to filter out the oxygen shell.
Result of curve fitting by BFBT (shown in dashed line) on Nb$_{0.7}$Ti$_{0.3}$O$_x$. The dashed line shown in the PRDF is the Hanning window applied to filter out the oxygen shell.
Result of curve fitting by BFBT (shown in daohsed line) on Nb_{0.8}Ti_{0.2}O_{2.5}. The dashed line shown in the PRDF is the Hanning window applied to filter out the oxygen shell.
Result of curve fitting by BFBT (shown in dashed line) on \( \text{Nb}_{0.9}\text{Ti}_{0.1}\text{O}_2 \). The dashed line shown in the PRDF is the Hanning window applied to filter out the oxygen shell.
Result of curve fitting by BFBT (shown in dashed line) on NbO$_3$. The dashed line shown in the PRDF is the Hanning window applied to filter out the oxygen shell.
Raw Data of DC Electrical Conductivity Measurement
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REFERENCES


