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# Coordination of Cations in $TiNb_2O_7$ by Raman Spectroscopy

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The Raman spectrum of the compound $TiNb_2O_7$ prepared by a liquid mix technique was recorded at room temperature using the 530.98-nm line from a krypton-ion laser as exciter. The bands observed at 998 and 884 $cm^{-1}$ are assigned to the edge-shared and corner-shared $NbO_6$ octahedra, respectively. The relative intensities of these two bands are consistent with the structure of $TiNb_2O_7$ worked out by earlier investigators using X-ray and neutron diffraction. The strong band observed at 647 $cm^{-1}$ is assigned to the vibration of the $TiO_6$ octahedra. The octahedral coordination for both cations based on the results of the Raman spectrum measurements is in essential agreement with the available structural data for the compound $TiNb_2O_7$. The weak band observed at 840 $cm^{-1}$ is suggestive of the presence of $NbO_4$ tetrahedra in small concentrations in $TiNb_2O_7$.

## Introduction

The phase equilibrium relations in the system $TiO_2$–$Nb_2O_5$ have been studied by Roth and Coughanour (*1*), who reported the existence of two binary compounds, $TiO_2 \cdot Nb_2O_5$ ($TiNb_2O_7$) and $TiO_2 \cdot 3Nb_2O_5$ ($TiNb_6O_{17}$). Wadsley (*2, 3*) studied the structure of $TiNb_2O_7$ and another compound, $2TiO_2 \cdot 5Nb_2O_5$ ($Ti_2Nb_{10}O_{29}$), by X-ray diffraction. Another compound with the formula $TiO_2 \cdot 12Nb_2O_5$ ($TiNb_{24}O_{62}$) was found to exist (*4*) on the $Nb_2O_5$-rich side of the system. Eror (*5*) identified the second phase formed in $TiO_2$ with 8 at.% $Nb^{5+}$ as $TiNb_2O_7$ when the samples were equilibrated in oxygen at 1060°C. Roth and Wadsley (*6*) determined the crystal structure of $TiNb_{24}O_{62}$ to be monoclinic with space group *C*2. They also reported the presence of metal atoms in tetrahedral coordination in $TiNb_{24}O_{62}$.

The structure of $TiNb_2O_7$ consists of rectangular blocks or columns of the $ReO_3$ type (*2, 3, 7, 8*). In $TiNb_2O_7$ (space group $A2/m$, $Z = 6$), each metal atom (Ti and Nb) is coordinated to six oxygens (*3, 8*) forming an octahedral grouping ($TiO_6$ and $NbO_6$). There is substantial ordering of the cations among the metal sites in $TiNb_2O_7$ (*8*). Roth and Wadsley (*6*) reported that there are no metal atoms in tetrahedral sites in $TiNb_2O_7$ and $Ti_2Nb_{10}O_{29}$. The reduction behavior of $TiNb_2O_7$ and $Ti_2Nb_{10}O_{29}$ has been studied recently by Forghany and Anderson (*9*). A brief summary of the Raman spectrum of $TiNb_2O_7$ is given by McConnell *et al.* (*10*). The present authors (*11*) investigated the vibrational spectra of the structural analog $TiTa_2O_7$. This work constitutes a study of the room-temperature Raman spectrum of $TiNb_2O_7$ prepared by a liquid mix technique.

## Experimental Procedure

The powder samples used in this investigation were prepared by a liquid mix tech-

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nique (*12–15*). This preparation technique is based upon having the individual cations complexed in separate weak organic acid solutions or available in salts that are soluble in the weak organic acid solution. The individual solutions or soluble salts are gravimetrically analyzed for the respective cation concentration to a precision of better than 10 ppm. In this way, it is possible to precisely control all of the cation concentrations and to mix the ions on an atomic scale in the liquid state. There is no precipitation in the mixed solutions as they are evaporated to the rigid polymeric state in the form of a uniformly colored transparent glass. Required amounts of niobium citrate solution prepared from niobium oxalate solution (Kawecki Berylco Industries) and tetraisopropyl titanate solution (Dupont Co., Tyzor) were mixed and the rigid polymeric glassy samples obtained by slow evaporation of the solution were calcined at 1200°C in air for 10 hr to get a white, crystalline powder. The Raman spectrum in the range 100–1250 $cm^{-1}$ was recorded at room temperature on a modified Jarrell-Ash 25-300 Raman spectrophotometer as described previously (*16–18*). The Raman spectrum was excited by the 530.98-nm line of a Spectra Physics Model 164 krypton-ion laser.

## Results and Discussion

The Raman spectrum of $TiNb_2O_7$ recorded at room temperature in the range 100–1240 $cm^{-1}$ is given in Fig. 1. McConnell *et al.* (*10*) reported that in the metal oxide systems containing niobium, titanium, or tungsten, the binding forces within the metal–oxygen octahedra are large compared to crystal binding forces. The internal vibrations of the $MO_6$ octahedra in these oxides should, therefore, be quite close to the free-ion modes. The external modes occur at considerably lower frequencies than the internal vibration modes and the high frequency Raman bands can be satisfactorily related to the cation–oxygen stretching modes (*10, 19*). The existence of a high-frequency band in the Raman spectrum points to the presence of a short cation–oxygen bond.

The $Nb^{5+}$ ion is reported to be too small to form regular $NbO_6$ octahedra in any oxide system (*20*). The ionic size is also too large to fit into an oxygen tetrahedron and this is probably the reason that $NbO_4$ tetra-

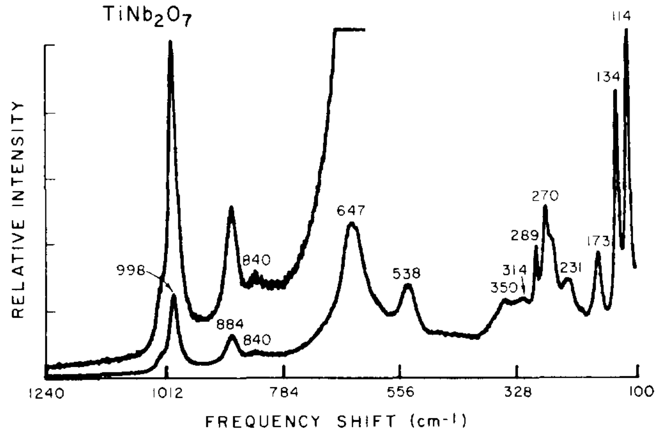

FIG. 1. Raman spectrum of powder samples of $TiNb_2O_7$ recorded at room temperature.

hedra very seldom occur in oxide systems (*21*). The metal atoms in niobium oxides form octahedra ($NbO_6$) that are distorted and share edges and corners (*10, 22*). Octahedral-site cations experience the largest mutual repulsive force if their octahedra share common faces, an intermediate repulsive force if they share corners or edges and the smallest repulsive force if they are isolated (*23*). Therefore, one cannot expect the $NbO_6$ octahedra in $TiNb_2O_7$ to be ideal with $O_h$ symmetry. These octahedra, however, will retain some elements of symmetry (e.g., $D_{4h}$, $C_{4v}$, $C_{3v}$, or $C_{2v}$) depending upon the extent of distortion.

According to Von Dreele and Cheetham (*8*), two types of octahedra, corner-shared and edge-shared, are present in the structure of $TiNb_2O_7$. Approximately 6/26 of the octrahedra are corner-shared and, according to Roth and Wadsley (*6*), there are no tetrahedral sites in the $TiNb_2O_7$ structure. There is substantial ordering of titanium ions (up to 64%) in the edge-shared octahedra. In oxide systems, the symmetric metal–oxygen stretching vibration, $\nu_1$ mode, is the most diagnostic one. In $TiNb_2O_7$, edge-shared $NbO_6$ octahedra have Nb–O distances between 1.66 and 2.38 Å with one-third less than 1.9 Å. The corner-shared octahedra are only slightly distorted. The bands observed at 998 and 884 $cm^{-1}$ are assigned to the vibrations of the $NbO_6$ octahedra since Raman bands are observed in this frequency range in various niobium-containing oxides (*10*). Since the edge-shared octahedra predominate over the corner-shared octahedra, the strong band observed at 998 $cm^{-1}$ in the present work is assigned to the vibrations of the edge-shared $NbO_6$ octahedra and the band at 884 $cm^{-1}$ to the corner-shared octahedra. The relative intensities of these two bands are in accord with the available structural data (*2, 3, 8*) for $TiNb_2O_7$. A significant observation of the present work is the weak band at 840 $cm^{-1}$ (see Fig. 1), which we believe is due to the $NbO_4$ tetrahedra in this compound. This assignment finds support from the strong Raman band observed at 830 $cm^{-1}$ in $YNbO_4$, one of the few niobium-containing compounds having $NbO_4$ tetrahedra (*21*). The intensity of the 840-$cm^{-1}$ band tentatively assigned to the $NbO_4$ tetrahedra is very low. The tetrahedral site for niobium atoms could be in the channel formed between the corners of the $ReO_3$-type blocks. Roth and Wadsley (*6*) have reported tetrahedral coordination for metal atoms in $TiNb_{24}O_{62}$. It is to be pointed out that the high-temperature form of $Nb_2O_5$ contains $ReO_3$-type blocks of two different sizes and one out of 28 niobium atoms occupy a tetrahedral site (*10, 22*). The present authors (*24*) have observed a weak band at 846 $cm^{-1}$ due to the $NbO_4$ tetrahedra in $Nb_2O_5$, thus confirming the observation of McConnell *et al.* (*10*).

The strong band observed at 647 $cm^{-1}$ is assigned to the vibrations of the edge-shared $TiO_6$ octahedra since the $Ti^{4+}$ ions preferentially occupy the edge-shared position. The band at 538 $cm^{-1}$ is also assigned to the $TiO_6$ octahedra and these assignments for the $TiO_6$ octahedra find support from the perovskites and $K_2NiF_4$-type compounds containing $TiO_6$ octahedra (*25–28*). These assignments must be confirmed by using isotopic substitution. There are many bands observed in the region <350 $cm^{-1}$. These bands are due to Nb–O and Ti–O vibrations and some of them are more probably due to complex motions involving the participation of both the cations. Raman bands below 200 $cm^{-1}$ are due to external modes. Metal–metal vibrations will give rise to Raman bands in this region.

In $TiNb_2O_7$ with space group $A2/m$ and $Z = 6$, there should be 87 ($3n - 3$, where $n = 30$) vibrational modes, because the unit cell contains two primitive cells, each with three formula units. In the point group $C_{2h}$, to which this compound supposedly belongs, the $A_g$ and $B_g$ modes are Raman active, whereas $A_u$ and $B_u$ modes are ir active. In close-coupled and polar substances, not all the predicted modes have been observed in the vibrational spectra. It is to be pointed out here that in the structural analog $TiTa_2O_7$, only 19 Raman bands and 10 infrared absorption bands were observed by the present authors (*11*). Many of the predicted modes may overlap or have very low polarizabilities. Since only a few of the predicted modes are observed, it is difficult to make firm classification of modes in these oxides. Isotopic substitution will help to distinguish the bands that are primarily due to Ti–O vibrations from the Nb–O modes.

The interpretation of the observed Raman spectrum on the basis of the presence of corner- and edge-shared octahedra in $TiNb_2O_7$ is in accord with the structure worked out by earlier investigators (*2, 3, 8*). Evidence presented in this work for the possible presence of $NbO_4$ tetrahedra in small concentrations warrants further investigation regarding the structure of $TiNb_2O_7$.

## Acknowledgment

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