

Presumably it was some GaSb-Ga mixture.

### Summary

The pyrolysis of TVSb has been investigated in a flow tube reactor using D<sub>2</sub> and He carrier gases. For TVSb alone, the most likely pyrolysis reaction involves an Sb-centered reductive elimination pathway. A less likely possibility is pyrolysis via homolysis of the Sb-C bonds, yielding vinyl radicals. Unfortunately, examination of the organic byproducts in both He and D<sub>2</sub> yields insufficient information to form a definitive hypothesis. However, in He the pyrolysis rate for TVSb is more rapid than for TMSb. Since vinyl radicals form stronger bonds than methyl radicals, this datum contradicts the Sb-C bond homolysis mechanism. Again, the activation energy for pyrolysis is less than the expected Sb-vinyl bond strength. Finally, the addition of C<sub>7</sub>D<sub>8</sub> produces no CH<sub>2</sub>=CHD,

indicative of the absence of vinyl radicals. To elucidate our understanding of GaSb growth by using TMGa and TVSb, the pyrolysis rates for this combination of reactants were also studied. CH<sub>3</sub> radicals from (CH<sub>3</sub>N)<sub>2</sub> pyrolysis were found to enhance TVSb pyrolysis in He. TMGa also increases the TVSb pyrolysis rate, mainly due to the methyl radicals produced. A heterogeneous pyrolysis reaction appears at high surface area. At V/III ratios normally used for OMVPE growth, carbonaceous deposits were formed. Thus, TVSb may be a useful precursor for OMVPE only at V/III ratios less than unity.

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**Registry No.** TVSb, 5613-68-3; TMGa, 1445-79-0.

## Structural Chemistry and Raman Spectra of Niobium Oxides

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A series of niobium oxide reference compounds were investigated by Raman spectroscopy in order to determine the relationship between niobium oxide structures and their corresponding Raman spectra. The assignments of the Raman bands were based on the known niobium oxide structures. The Raman studies indicate that the Raman frequencies strongly depend on the niobium oxide structures. For the slightly distorted octahedral NbO<sub>6</sub> structures (KNbO<sub>3</sub>, NaNbO<sub>3</sub>, and LiNbO<sub>3</sub>), the major Raman frequencies appear in the 500-700-cm<sup>-1</sup> region. For the highly distorted octahedral NbO<sub>6</sub> structures (K<sub>8</sub>Nb<sub>6</sub>O<sub>19</sub>, AlNbO<sub>4</sub>, and Nb(HC<sub>2</sub>O<sub>4</sub>)<sub>5</sub>), the major Raman frequencies shift from the 500-700- to the 850-1000-cm<sup>-1</sup> region. The distortions in the niobium oxide compounds are caused by the corner- or edge-shared NbO<sub>6</sub> octahedra. Both slightly distorted and highly distorted octahedral NbO<sub>6</sub> sites coexist in the KCa<sub>2</sub>Na<sub>n-3</sub>Nb<sub>n</sub>O<sub>3n+1</sub>, *n* = 3-5, layered compounds. Most of the niobium oxide compounds possess an octahedrally coordinated NbO<sub>6</sub> structure with different extents of distortion, and only a few rare-earth ANbO<sub>4</sub> (A = Y, Yb, Sm, and La) compounds possess a tetrahedrally coordinated NbO<sub>4</sub> structure. For the tetrahedral NbO<sub>4</sub> structure of YbNbO<sub>4</sub> the major Raman frequency appears at ~813 cm<sup>-1</sup>. In situ Raman studies assisted in the discrimination between bulk and surface functionalities in the niobium oxide reference compounds possessing high surface areas (Nb<sub>2</sub>O<sub>5</sub>·*n*H<sub>2</sub>O and HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub>).

### Introduction

Niobium oxide, Nb<sub>2</sub>O<sub>5</sub>, has been reported to exist in different polymorphic forms,<sup>1-4</sup> and the phase transformations of niobium oxide strongly depend on the heat treatment. Upon heat treatments between 300 and 1000 °C, amorphous niobium oxide increases in degree of crystallinity and forms more stable Nb<sub>2</sub>O<sub>5</sub> phases. Amorphous niobium oxide, Nb<sub>2</sub>O<sub>5</sub>·*n*H<sub>2</sub>O, possesses distorted NbO<sub>6</sub> octahedra, NbO<sub>7</sub> pentahedra, and NbO<sub>8</sub> hexahedra as structural units.<sup>5</sup> The TT-Nb<sub>2</sub>O<sub>5</sub> phase, 300-500 °C, possesses a pseudo-hexagonal unit cell, with a constitutional defect of an oxygen atom per unit cell, and forms tetragonal and pentagonal bipyramids<sup>1</sup> with six or

seven oxygen atoms coordinated to the Nb atom. The T-Nb<sub>2</sub>O<sub>5</sub> phase, 700-800 °C, possesses an orthorhombic unit cell and forms distorted tetragonal or pentagonal bipyramids with six or seven oxygen atoms coordinated to the Nb atom. One out of seventeen Nb atoms occupies the interstitial sites between two unit cells and is surrounded by eight oxygen atoms.<sup>6</sup> These polyhedra are joined by corner or edge sharing in the *ab* plane and by corner sharing along the *c* axis. The H-Nb<sub>2</sub>O<sub>5</sub> phase, above 1000 °C, is the most thermodynamically stable form of the Nb<sub>2</sub>O<sub>5</sub> polymorphs. The structure of H-Nb<sub>2</sub>O<sub>5</sub> contains two different sizes of ReO<sub>3</sub>-type blocks: 3 × 4 and 3 × 5 blocks composed of corner- or edge-shared NbO<sub>6</sub> octahedra. Only 1 out of 28 Nb sites is a tetrahedron.<sup>7</sup>

The niobium oxide structure can be modified by cation substitution into the crystalline lattice to form different kinds of niobium oxide compounds: perovskite structure,<sup>8-10</sup> layered structure,<sup>11-13</sup> and Nb<sub>6</sub>O<sub>19</sub><sup>8-</sup> clusters.<sup>14-16</sup>

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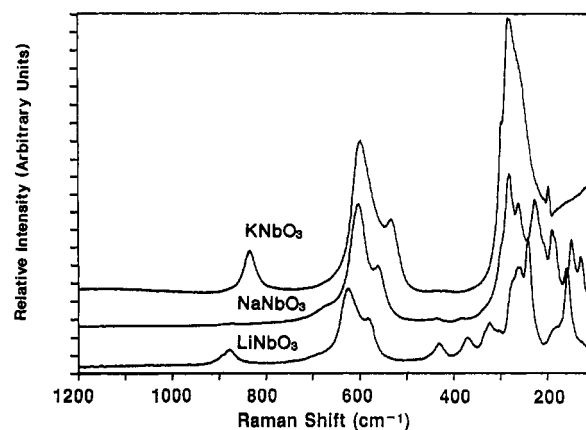
These modifications enhance the physical and chemical properties of niobium oxide. The perovskite niobium oxide compounds are used in various fields of materials science such as glasses<sup>17,18</sup> and ceramics,<sup>19,20</sup> and the layered niobium oxide compounds undergo intercalation reactions with organic amines.<sup>21</sup>  $\text{Nb}_2\text{O}_5$  also reacts with oxalic acid to form niobium oxalate complexes which can exist in aqueous solution.<sup>22</sup> The above niobium oxide compounds possess an octahedrally coordinated  $\text{NbO}_6$  structure with different extents of distortion. The tetrahedrally coordinated  $\text{NbO}_4$  structure is not a typical structure for niobium oxide because the  $\text{Nb}^{5+}$  atom is too large to fit into an oxygen-anion tetrahedron. Only a few rare-earth  $\text{ANbO}_4$  ( $A = \text{Y, Yb, Sm, and La}$ ) compounds have been found to possess tetrahedral coordination.<sup>23-25</sup>

Raman spectroscopy is very sensitive to the structure and bond order of metal oxides, especially in the region of metal-oxygen stretching modes, because many of the Raman frequencies depend on the bond order in the structure.<sup>3</sup> A higher metal-oxygen bond order, corresponding to a shorter bond distance, shifts the Raman bond to higher wavenumbers. In this study, various niobium oxide reference compounds are characterized by Raman spectroscopy and divided into two main categories: the octahedrally coordinated and the tetrahedrally coordinated niobium oxide compounds. The octahedrally coordinated niobium oxide compounds consist of slightly distorted niobium oxides, highly distorted niobium oxide structures, layered structures, and pure niobium oxide. Tetrahedrally coordinated  $\text{ANbO}_4$  ( $A = \text{Y, Yb, Sm, and La}$ ) compounds have been reported by Blasse,<sup>23</sup> Rooksby et al.,<sup>24</sup> and Yoshida et al.<sup>25</sup> to possess a slightly distorted scheelite structure with  $\text{NbO}_4$  units, and only  $\text{YNbO}_4$  has previously been characterized by Raman spectroscopy. In the present study  $\text{YbNbO}_4$  was used as the niobium oxide reference compound containing a tetrahedrally coordinated  $\text{NbO}_4$  structure. The niobium oxide structure-Raman spectroscopy relationships developed for the reference compounds will subsequently be used to assign the molecular structures of the surface niobium oxide phases in supported niobium oxide catalysts.

## Experimental Section

**Materials.** Hydrated niobium pentoxide,  $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ , was

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**Figure 1.** Raman spectra of the  $\text{BNbO}_3$  ( $B = \text{Li, Na, K}$ ) compounds.

provided by Niobium Products Co. (Pittsburgh, PA) with a minimum purity of 99.0%. The major impurities after calcining at 800 °C are 0.02% Ta and 0.01% Cl. Niobium oxalate was also provided by Niobium Products Co. with the chemical analysis of 20.5%  $\text{Nb}_2\text{O}_5$ , 790 ppm Fe, 680 ppm Si, and 0.1% insoluble solid.

The  $\text{BNbO}_3$  ( $B = \text{Li, Na, and K}$ ) compounds were obtained from Johnson Matthey Chemicals Co. with a purity greater than 99.99%. Potassium niobate,  $\text{K}_8\text{Nb}_6\text{O}_{19}$ , was obtained from Pfaltz and Bauer, Inc. The  $\text{KCa}_2\text{Na}_{n-3}\text{Nb}_n\text{O}_{3n+1}$  ( $n = 3-5$ ) compounds were provided by A. Jacobson of Exxon Research and Engineering Co.; the detailed synthesis procedures of these layered oxides were described by Jacobson et al.<sup>13</sup> The hydrated  $\text{HCa}_2\text{Nb}_3\text{O}_{10}$  layered oxide was also provided by A. Jacobson. The dehydrated  $\text{H-Ca}_2\text{Nb}_3\text{O}_{10}$  layered oxide was prepared by drying the hydrated  $\text{H-Ca}_2\text{Nb}_3\text{O}_{10}$  layered oxide at 120 °C for 16 h.

**BET Surface Area Measurement.** The BET surface areas of bulk niobium oxide samples were obtained with a Quantorb surface area analyzer (Quantachrome Corp. Model OS-9) using a 3:7 ratio of  $\text{N}_2/\text{He}$  mixture as a probe gas. Typically, 0.200–0.300 g of sample was used for the measurement, and the sample was outgassed at 250 °C prior to  $\text{N}_2$  adsorption.

**Raman Spectroscopy.** Raman spectra were obtained with a Spex triplemate spectrometer (Model 1877) coupled to an EG&G intensified photodiode array detector, which were cooled thermoelectrically to -35 °C, and interfaced with an EG&G OMA III optical multichannel analyzer (Model 1463). The samples were excited by the 514.5-nm line of the  $\text{Ar}^+$  laser with 10 mW of power. The laser beam was focused on the sample illuminator, where the sample typically spins at about 2000 rpm to avoid local heating, and is reflected into the spectrometer by a 90° angle with the incident light. The scattered Raman light was collected by the spectrometer at room temperature and analyzed with an OMA III software package. The overall spectral resolution of the spectra was determined to be about 2  $\text{cm}^{-1}$ . The detailed schematic diagram of the Raman spectrometer is described elsewhere.<sup>26</sup>

An in situ quartz cell was designed in order to investigate the Raman changes upon dehydration of the niobium oxide samples above room temperature. The sample holder was made from a quartz glass, and the sample disk was held by a stationary slot in the sample holder. The sample was heated by a cylindrical heating coil surrounding the quartz cell, and the temperature was measured with an internal thermocouple. The cell was capable of operating up to 600 °C. Reaction gas mixtures were introduced into the cell from a manifold at a rate of 50–500  $\text{cm}^3/\text{min}$  with a delivery pressure of 150–200 Torr.

## Results

**(a) Octahedrally Coordinated Niobium Oxide Compounds. Slightly distorted niobium oxides:** The Raman spectra of the  $\text{BNbO}_3$  ( $B = \text{Li, Na, and K}$ ) reference compounds are shown in Figure 1. The major Raman

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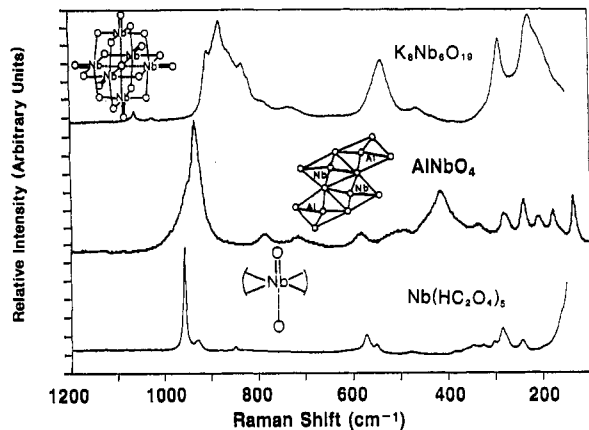


Figure 2. Raman spectra of the highly distorted niobium oxide compounds.

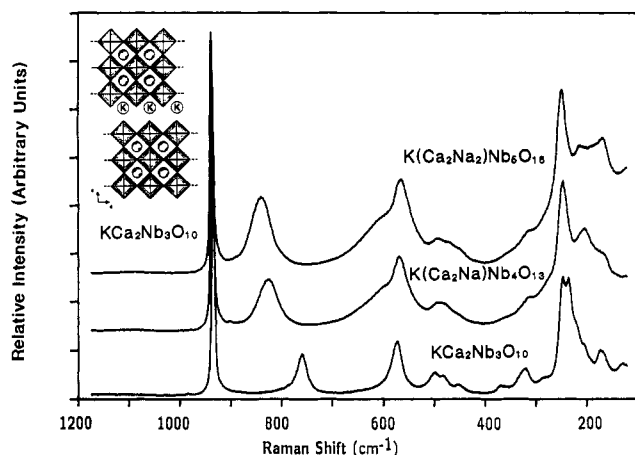


Figure 3. Raman spectra of the  $\text{KCa}_2\text{Na}_{n-3}\text{Nb}_n\text{O}_{3n+1}$  ( $n = 3-5$ ) layered oxide compounds.

band of these reference compounds appears in the 620–630- $\text{cm}^{-1}$  region, and a shoulder appears in the 520–580- $\text{cm}^{-1}$  region. The  $\text{LiNbO}_3$  compound possesses additional Raman bands at  $\sim 870$ ,  $\sim 430$ ,  $\sim 375$ , and  $\sim 325$   $\text{cm}^{-1}$ . However, the intensity of these Raman bands is significantly decreased for the  $\text{NaNbO}_3$  compound and are essentially absent for the  $\text{KNbO}_3$  compound. For the  $\text{KNbO}_3$  compound, an additional Raman band is observed at  $\sim 840$   $\text{cm}^{-1}$ . Multiple and strong Raman bands in the low-wavenumber region, between 100 and 300  $\text{cm}^{-1}$ , are also observed for these reference compounds.

**Highly distorted niobium oxides:** The Raman spectra of the  $\text{K}_8\text{Nb}_6\text{O}_{19}$ ,  $\text{AlNbO}_4$ , and  $\text{Nb}(\text{HC}_2\text{O}_4)_5$  reference compounds are shown in Figure 2. In the high-wavenumber region (800–1000  $\text{cm}^{-1}$ ),  $\text{K}_8\text{Nb}_6\text{O}_{19}$  possesses Raman bands at  $\sim 900$ ,  $\sim 880$ , and  $\sim 840$   $\text{cm}^{-1}$ ,  $\text{AlNbO}_4$  has a Raman band at  $\sim 930$   $\text{cm}^{-1}$ , and  $\text{Nb}(\text{HC}_2\text{O}_4)_5$  possesses a Raman band at  $\sim 960$   $\text{cm}^{-1}$ . In the intermediate-wavenumber region (400–800  $\text{cm}^{-1}$ ), the major Raman band of these niobium oxide compounds appears at  $\sim 540$  ( $\text{K}_8\text{Nb}_6\text{O}_{19}$ ),  $\sim 420$  ( $\text{AlNbO}_4$ ), and  $\sim 570$  ( $\text{Nb}(\text{HC}_2\text{O}_4)_5$ ). Additional Raman bands at  $\sim 580$ ,  $\sim 730$ , and  $\sim 780$   $\text{cm}^{-1}$  are observed for  $\text{AlNbO}_4$ . In the low-wavenumber region (100–300  $\text{cm}^{-1}$ ),  $\text{K}_8\text{Nb}_6\text{O}_{19}$  and  $\text{Nb}(\text{HC}_2\text{O}_4)_5$  have Raman bands at  $\sim 230$  and  $\sim 290$   $\text{cm}^{-1}$  and  $\text{AlNbO}_4$  has Raman bands at  $\sim 275$ ,  $\sim 240$ ,  $\sim 210$ , and  $\sim 180$   $\text{cm}^{-1}$ .

**Layered oxides:** The Raman spectra of the  $\text{KCa}_2\text{Na}_{n-3}\text{Nb}_n\text{O}_{3n+1}$  ( $n = 3-5$ ) layered oxide reference compounds are presented in Figure 3. The major Raman band of these layered oxides appears at  $\sim 930$   $\text{cm}^{-1}$ . Additional Raman bands at  $\sim 760$ ,  $\sim 575$ , and 300–500  $\text{cm}^{-1}$

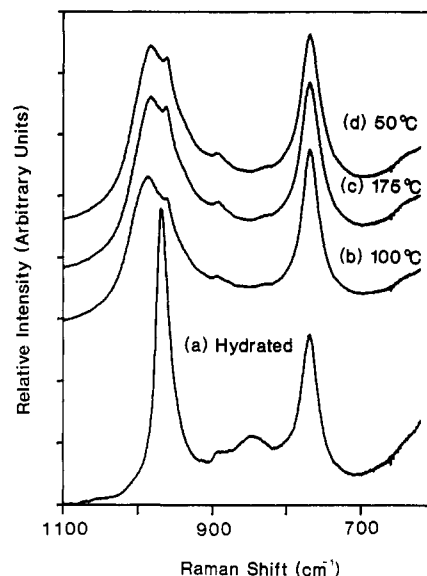


Figure 4. In situ Raman spectra of the  $\text{HCa}_2\text{Nb}_3\text{O}_{10}$  layered oxide compound: (a) hydrated state; (b) heated at 100 °C under flowing oxygen; (c) heated at 175 °C under flowing oxygen; (d) cooled to 50 °C under flowing oxygen.

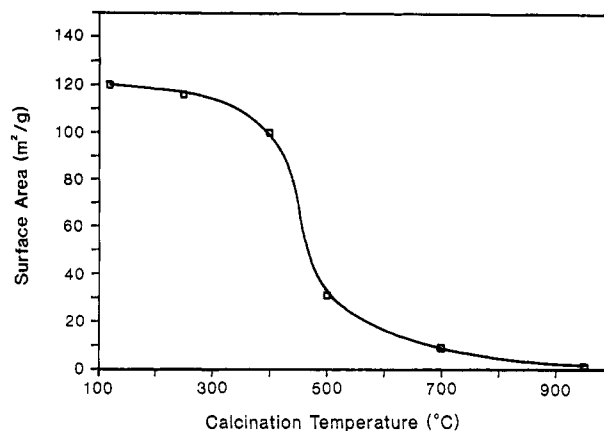
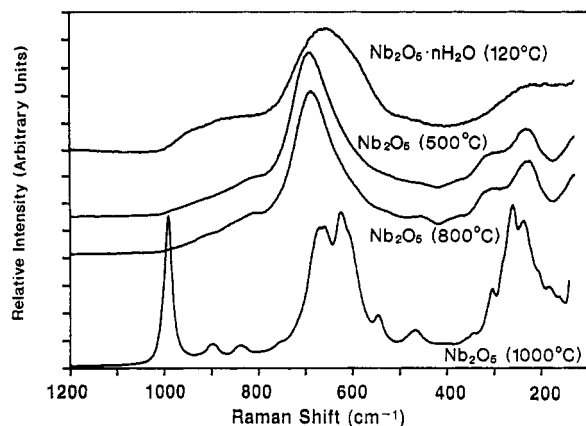


Figure 5. Surface area of bulk niobium oxide as a function of calcination temperature.

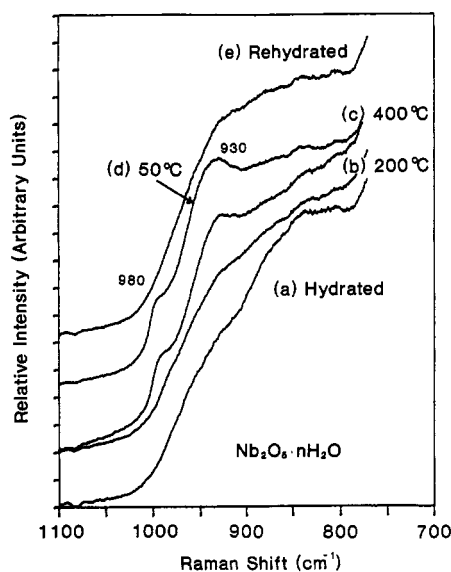
are also present for the  $\text{KCa}_2\text{Nb}_3\text{O}_{10}$  compound. A shift of the Raman band from  $\sim 760$  to  $\sim 825$   $\text{cm}^{-1}$  is observed upon increasing the number of layers from three to four, and this band further shifts to  $\sim 840$   $\text{cm}^{-1}$  as the number of layers is increased to five. The Raman bands at  $\sim 450$  and  $\sim 375$   $\text{cm}^{-1}$  disappear for the compounds possessing three and four layers.

The dehydrated state of the  $\text{HCa}_2\text{Nb}_3\text{O}_{10}$  layered oxide was investigated by in situ Raman spectroscopy under flowing oxygen, and the results are shown in Figure 4. The  $\sim 930$ - $\text{cm}^{-1}$  Raman band for the  $\text{KCa}_2\text{Nb}_3\text{O}_{10}$  compound, Figure 3, shifts to  $\sim 965$   $\text{cm}^{-1}$  for the hydrated  $\text{HCa}_2\text{Nb}_3\text{O}_{10}$  compound. Upon dehydration, the strong Raman band at  $\sim 965$   $\text{cm}^{-1}$  splits into two bands at  $\sim 980$  and  $\sim 960$   $\text{cm}^{-1}$ , and the weak Raman band at  $\sim 840$   $\text{cm}^{-1}$  disappears.

**Bulk niobium oxide ( $\text{Nb}_2\text{O}_5$ ):** The surface area of bulk niobium oxide after different thermal treatments is presented in Figure 5. The results show that the niobium oxide surface area dramatically decreases with increasing calcination temperature due to the formation of larger  $\text{Nb}_2\text{O}_5$  crystallites. The Raman spectra of bulk niobium oxide after thermal treatments from 120 to 1000 °C are shown in Figure 6. For  $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  dried at 120 °C for 16 h, a broad and weak Raman band is observed at  $\sim 900$   $\text{cm}^{-1}$  as well as a broad and strong Raman band at  $\sim 650$

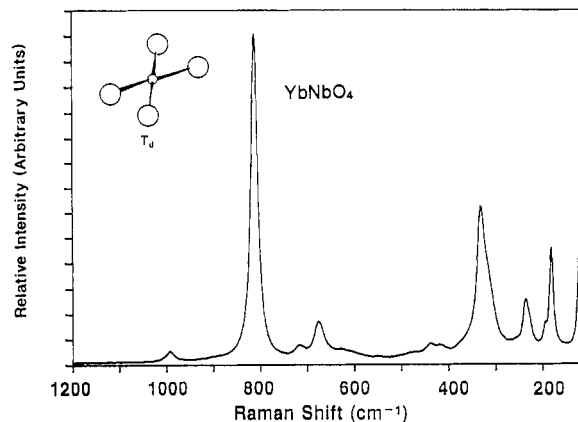


**Figure 6.** Raman spectra of bulk niobium oxide as a function of calcination temperatures.




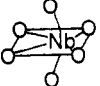

**Figure 7.** In situ Raman spectra of  $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ : (a) hydrated state; (b) heated at 200 °C under flowing oxygen; (c) heated at 400 °C under flowing oxygen; (d) cooled to 50 °C under flowing oxygen; (e) reabsorbed water molecules under ambient conditions.

$\text{cm}^{-1}$ . When the niobium oxide sample is heated for 2 h at 500 °C in air, the broad Raman band at  $\sim 900 \text{ cm}^{-1}$  becomes even weaker and the strong Raman band at  $\sim 650 \text{ cm}^{-1}$  shifts to  $\sim 690 \text{ cm}^{-1}$ . The  $\text{Nb}_2\text{O}_5$  (500 °C) Raman bands in the low-wavenumber region ( $200\text{--}300 \text{ cm}^{-1}$ ) become more intense and better resolved than those of  $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  (120 °C) in this region. The Raman features of the  $\text{Nb}_2\text{O}_5$  sample treated at 800 °C for 2 h are similar to those of the  $\text{Nb}_2\text{O}_5$  (500 °C) sample. However, additional weak Raman bands in the  $400\text{--}500\text{-cm}^{-1}$  region are observed in the  $\text{Nb}_2\text{O}_5$  (800 °C) sample. For the  $\text{Nb}_2\text{O}_5$  sample treated at 1000 °C for 2 h, the Raman results indicate that a phase transformation of the  $\text{Nb}_2\text{O}_5$  sample has occurred and additional Raman bands are observed in the spectrum (particularly in the high-wavenumber region between 900 and  $1000 \text{ cm}^{-1}$ ). The different  $\text{Nb}_2\text{O}_5$  phases are also confirmed by X-ray diffraction.<sup>27</sup>  $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  (120 °C) is found to be poorly crystalline, showing a diffuse pattern of either monoclinic  $\text{Nb}_2\text{O}_5$  or  $\text{NbO}_{2.432}$  (oxygen-deficient  $\text{Nb}_2\text{O}_5$ ).  $\text{Nb}_2\text{O}_5$  (500 °C) and  $\text{Nb}_2\text{O}_5$  (800 °C) are similar, matching well-crystalline orthorhombic  $\text{Nb}_2\text{O}_5$ .  $\text{Nb}_2\text{O}_5$  (1000 °C) is very crystalline as well, indicating a mixture of monoclinic phases of  $\text{Nb}_2\text{O}_5$ .



**Figure 8.** Raman spectrum of the  $\text{YbNbO}_4$  compound.

**Table I. Relationships between Niobium Oxide Structures and Raman Frequencies**

struct	Raman bands, $\text{cm}^{-1}$	compounds
	790–830	$\text{YNbO}_4$ , $\text{YbNbO}_4$
	500–700	$\text{Nb}_2\text{O}_5$ (amorphous, TT, T, and H), $\text{LiNbO}_3$ , $\text{NaNbO}_3$ , $\text{KNbO}_3$ , layered oxides
	850–1000	$\text{AlNbO}_4$ , $\text{K}_8\text{Nb}_6\text{O}_{19}$ , $\text{Nb}(\text{HC}_2\text{O}_4)_5$ , layered oxides

In situ Raman studies of the high surface area  $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  (120 °C) sample were also undertaken in order to discriminate between bulk and surface functionalities,<sup>26</sup> and the spectra in the  $700\text{--}1100\text{-cm}^{-1}$  region are presented in Figure 7. For the untreated  $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  (120 °C), a broad Raman band is observed in the  $800\text{--}900\text{-cm}^{-1}$  region. For the  $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  (120 °C) treated at 200 °C for 1 h, the Raman features remain broad and are somewhat similar to the untreated  $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  (120 °C). Two new Raman bands, however, are observed at  $\sim 930$  and  $\sim 980 \text{ cm}^{-1}$  after thermal treatment at 400 °C for 1 h. These two Raman bands are still present after cooling to 50 °C. However, these two Raman bands disappear after the sample is rehydrated by exposure to ambient water vapor overnight. The major niobium oxide Raman band remained at  $\sim 650 \text{ cm}^{-1}$  during this thermal treatment and indicates that the  $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  sample did not undergo phase transformations.

**(b) Tetrahedrally Coordinated Niobium Oxide Compound.** The Raman spectrum of  $\text{YbNbO}_4$  is shown in Figure 8. Raman studies reveal that  $\text{YbNbO}_4$  possessing Raman bands at  $\sim 813$ ,  $\sim 331$ ,  $\sim 717$ , and  $\sim 435 \text{ cm}^{-1}$ . Raman bands at  $\sim 992$ ,  $\sim 678$ ,  $\sim 630$ , and  $\sim 237 \text{ cm}^{-1}$  indicate that  $\text{YbNbO}_4$  also possesses a structure similar to that of  $\text{H-Nb}_2\text{O}_5$  (see Figure 6). The Raman bands below  $200 \text{ cm}^{-1}$  are due to lattice vibrations.

### Discussion

Most of the niobium oxide compounds contain an octahedral  $\text{NbO}_6$  structure with different extents of distortions present in the structures. Niobium oxide compounds containing a tetrahedral  $\text{NbO}_4$  structure are extremely rare. The major Raman frequencies of the niobium oxide compounds with the corresponding structures are classified in Table I. A higher niobium–oxygen bond order, corre-

(27) Jehng, J. M.; McCaslin, P. C.; Wachs, I. E., to be published.

sponding to a shorter bond distance, shifts the Raman band to higher wavenumbers. Every niobium oxide compound in this study has a unique Raman spectrum that is related to the symmetry and bond order of its structure. The Raman band assignments are based on the corresponding Nb–O bond order and known structure.

The tetrahedral NbO<sub>4</sub><sup>3-</sup> species does not exist in aqueous solutions because of the high electronegativity and small radius of the oxygen atom.<sup>28</sup> In addition, the tetrahedral NbO<sub>4</sub> structure is rarely found in niobium oxide compounds because the Nb<sup>5+</sup> atom is usually too large to fit into an oxygen-anion tetrahedron.<sup>23</sup> The rare-earth ANbO<sub>4</sub> (A = Y, Sm, and La) compounds have been investigated by Blasse<sup>23</sup> and Rooksby et al.,<sup>24</sup> and they determined that these compounds possess NbO<sub>4</sub> tetrahedra that appear to be isomorphous with the scheelite CaWO<sub>4</sub> structure. Blasse<sup>23</sup> studied the YNbO<sub>4</sub> compound by Raman spectroscopy and predicted the vibrational modes of a regular NbO<sub>4</sub> tetrahedron with no interactions and distortions to occur at 816 ( $\nu_1$ ), 650 ( $\nu_3$ ), 420 ( $\nu_4$ ), and 340 cm<sup>-1</sup> ( $\nu_2$ ). Yoshida et al.<sup>25</sup> investigated the YbNbO<sub>4</sub> compound by XANES and EXAFS techniques and determined that the YbNbO<sub>4</sub> compound possesses a NbO<sub>4</sub> tetrahedron. The ANbO<sub>4</sub> (A = Y, Yb, Sm, and La) compounds were further studied by Kinzhbalo et al.<sup>29</sup> and Trunov et al.,<sup>30</sup> who determined that these compounds possess a fergusonite structure at room temperature. In the fergusonite structure, the coordination number of the Nb atom contains four oxygen atoms with distances of 1.83–1.93 Å and two further oxygen atoms with distances of 2.40–2.52 Å as a result of the connection between two adjacent tetrahedra. The transition from the octahedral fergusonite to the tetrahedral scheelite depends on temperature. An increase in temperature results in bonds breaking between the niobium atom and the two further oxygen atoms, and the Nb atom coordination becomes tetrahedral.

For the ANbO<sub>4</sub> (A = Y, Yb, Sm, and La) compounds, the transition temperature from the octahedral fergusonite to the tetrahedral scheelite depends on the ionic radius of the rare-earth metal. The rare-earth metal possessing a small ionic radius has a high phase transition temperature because of the relatively short bond distances between the niobium atom and the two further oxygen atoms. Thus, the rare-earth ANbO<sub>4</sub> (A = Y, Yb, Sm, and La) compounds possess NbO<sub>6</sub> octahedra at room temperature, and transition from a NbO<sub>6</sub> octahedron to a NbO<sub>4</sub> tetrahedron occurs at high temperature. For example, the phase transitions of the YNbO<sub>4</sub> and the YbNbO<sub>4</sub> compounds occur above 825 °C.<sup>30</sup> Blasse<sup>23</sup> did not address the YNbO<sub>4</sub> structures as a function of temperature. The multiple Raman bands appearing in the 400–800-cm<sup>-1</sup> region for the YNbO<sub>4</sub> compound reported by Blasse<sup>23</sup> are probably due to the simultaneous presence of NbO<sub>4</sub> tetrahedra and NbO<sub>6</sub> octahedra in the structure.

Raman studies of the annealed YbNbO<sub>4</sub> compound reveal bands at ~813, ~717, ~435, and ~331 cm<sup>-1</sup>. The Raman bands appearing at ~813 and ~331 cm<sup>-1</sup> are due to the Nb–O symmetric modes of the NbO<sub>4</sub> tetrahedral structure, and Raman bands appearing at ~717 and ~435 cm<sup>-1</sup> are due to the Nb–O antisymmetric modes of the NbO<sub>4</sub> tetrahedral structure. This is consistent with Blasse's results that the vibrational modes of a regular NbO<sub>4</sub> tetrahedra, with no interactions and distortions,

should occur at 816 ( $\nu_1$ ), 650 ( $\nu_3$ ), 420 ( $\nu_4$ ), and 340 cm<sup>-1</sup> ( $\nu_2$ ).<sup>23</sup> Additional weak Raman bands appearing at ~992, ~678, ~630, and ~237 cm<sup>-1</sup> indicate that the YbNbO<sub>4</sub> compound also contains an impurity of H-Nb<sub>2</sub>O<sub>5</sub> due to a small excess of niobium oxide in the sample. Thus, tetrahedrally coordinated niobium oxide reference compounds possess their major Raman bands in the 790–830-cm<sup>-1</sup> region.

It appears that the Nb<sup>5+</sup> is also too small to form a regular octahedral NbO<sub>6</sub> structure,<sup>31</sup> and the oxygens in a regular octahedral NbO<sub>6</sub> structure do not obey Pauling's electrostatic valence rule.<sup>32</sup> Consequently, the niobium oxide compounds predominantly contain NbO<sub>6</sub> octahedra with different extents of distortion due to corner or edge-shared NbO<sub>6</sub> polyhedra.

The BNbO<sub>3</sub> (B = Na and K) compounds belong to the perovskite structure family. The Nb atom lies at each corner of a cubic cell, and the oxygen atom lies at the center of each cubic edge. Each Nb atom is surrounded by six oxygen atoms to form a NbO<sub>6</sub> octahedron and two adjacent NbO<sub>6</sub> octahedra are connected by a shared corner. The cation (Na or K) lies in the center of the cubic cell. In an ideal perovskite structure all NbO<sub>6</sub> octahedra would be perfectly regular with the cation (Na or K) surrounded by 12 oxygens and Nb by 6 oxygens. However, such an ideal perovskite structure does not exist in the BNbO<sub>3</sub> (B = Na and K) compounds because of the tilting of the NbO<sub>6</sub> octahedra as well as the displacements of the Nb atoms from the center which is induced by the cation (Na or K) and the unbalanced interatomic forces present in the perovskite structures.<sup>8</sup>

The perovskite BNbO<sub>3</sub> (B = Na and K) compounds possess a major Raman band at 620–630 cm<sup>-1</sup> and a shoulder in the 520–580-cm<sup>-1</sup> region (Figure 1). These bands correspond to slightly different Nb–O bond distances and are assigned to the symmetric stretching mode of the NbO<sub>6</sub> octahedra of these perovskite compounds. The LiNbO<sub>3</sub> compound contains a hexagonal close-packed structure in which the regular NbO<sub>6</sub> octahedra are connected by shared corners with a 30° tilting angle between two adjacent NbO<sub>6</sub> octahedra and a 0.26 Å off-center displacement of the Nb atom.<sup>8</sup> The LiNbO<sub>3</sub> compound possesses similar Raman features as the perovskite BNbO<sub>3</sub> (B = Na and K) compounds in the 500–700-cm<sup>-1</sup> region. For the LiNbO<sub>3</sub> (hexagonal close packing) Raman spectrum, the additional Raman band at ~870 cm<sup>-1</sup> is assigned to the antisymmetric stretching mode of the Nb–O–Nb linkage, and the associated bending modes of the Nb–O–Nb linkage appear at ~430 and ~375 cm<sup>-1</sup>. For the NaNbO<sub>3</sub> (perovskite) compound, however, the intensity of the Raman bands at ~870, ~430, and ~375 cm<sup>-1</sup> significantly decrease. This is probably due to the lower tilt angle, 18°, between the adjacent NbO<sub>6</sub> octahedra.<sup>9</sup> Furthermore, the disappearance of these Raman bands in the KNbO<sub>3</sub> (perovskite) Raman spectrum suggests that no tilting occurs between the adjacent NbO<sub>6</sub> octahedra in this structure and is consistent with Katz et al.'s results.<sup>10</sup> A new Raman band is observed at ~840 cm<sup>-1</sup> for KNbO<sub>3</sub>, which is characteristic of the symmetric stretching mode of the Nb–O–Nb collinear bond present in the structure. The distortions of the BNbO<sub>3</sub> (B = Li, Na, and K) compounds depend on the size of the A cations. For the larger size cation such as K the cation is coordinated to 12 oxygens, and free space is unavailable for the NbO<sub>6</sub> octahedra

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to tilt relative to one another. Consequently, the  $\text{NbO}_6$  octahedra maintain the parallel orientation. However, the smaller size Li cation only has six coordinated oxygens and forms an octahedral  $\text{LiO}_6$  structure. The orientations of the  $\text{NbO}_6$  and  $\text{LiO}_6$  octahedra induce the tilting between the two adjacent  $\text{NbO}_6$  octahedra.<sup>8</sup>

It is known that niobium oxide can exist as  $\text{Nb}_6\text{O}_{19}^{8-}$  clusters in alkaline aqueous solutions and Nb complexes in acidic aqueous solutions as well as precipitates from such solutions. The  $\text{Nb}_6\text{O}_{19}^{8-}$  unit is a well-characterized structure that consists of three different types of Nb-O bonds at each niobium center (see Figure 2): a short Nb=O terminal double bond, a longer Nb-O-Nb bridging bond, and a very long and weak Nb---O bond connected to the center of the cage-like octahedral structure.<sup>14-16</sup> From the known structure of  $\text{K}_8\text{Nb}_6\text{O}_{19}$ , the main frequencies of the  $\text{K}_8\text{Nb}_6\text{O}_{19}$  Raman spectrum in Figure 2 can be assigned: Nb=O terminal stretching mode ( $\sim 900$ ,  $\sim 880$ , and  $\sim 840$   $\text{cm}^{-1}$ ), edge-shared octahedral  $\text{NbO}_6$  stretching mode ( $\sim 730$ ,  $\sim 540$ , and  $\sim 460$   $\text{cm}^{-1}$ ), Nb---O stretching mode ( $\sim 290$   $\text{cm}^{-1}$ ), and Nb-O-Nb bending mode ( $\sim 230$   $\text{cm}^{-1}$ ). The multiple terminal stretching modes present in the high-wavenumber region are due to unequal Nb=O bond lengths that are present in the  $\text{K}_8\text{Nb}_6\text{O}_{19}$  structure.

The niobium oxalate structure consists of a  $[\text{NbO}(\text{OH})(\text{C}_2\text{O}_4)_2\text{H}_2\text{O}]$  or  $[\text{NbO}(\text{C}_2\text{O}_4)_3]$  unit and water molecules connected by hydrogen bonds.<sup>33-36</sup> The presence of different niobium oxalate units is dependent on the preparation methods. The  $[\text{NbO}(\text{OH})(\text{C}_2\text{O}_4)_2\text{H}_2\text{O}]$  unit has a pentagonal bipyramidal structure with a short Nb=O terminal double bond and a long Nb-OH<sub>2</sub> bond nearly perpendicular to the pentagonal equatorial plane which consists of two bidentate oxalato ligands and a hydroxyl group. The  $[\text{NbO}(\text{C}_2\text{O}_4)_3]$  unit also has a pentagonal bipyramidal structure with a short Nb=O terminal double bond and three bidentate oxalato ligands coordinated to the pentagonal equatorial plane. The sharp and strong Raman band at  $\sim 960$   $\text{cm}^{-1}$  in the niobium oxalate Raman spectrum is assigned to the Nb=O terminal double bond, and the Raman band at  $\sim 290$   $\text{cm}^{-1}$  is assigned to the long and weak Nb-OH<sub>2</sub> bond. The Raman band at  $\sim 570$   $\text{cm}^{-1}$  arises from the bidentate oxalato ligands coordinated to the niobium atom which is characteristic of the breathing mode of the Nb-O<sub>2</sub>-C<sub>2</sub> bridging bond.

The structure of  $\text{AlNbO}_4$  consists of highly distorted octahedral  $\text{NbO}_6$  and  $\text{AlO}_6$ , two  $\text{NbO}_6$  units and two  $\text{AlO}_6$  units, sharing edges together to form a unit cell and linked to the adjacent unit cell by sharing two corners.<sup>37</sup> The Nb-O bond which links to the adjacent unit cell by sharing two corners possesses the shortest bond length, and the Raman band at  $\sim 930$   $\text{cm}^{-1}$  is characteristic of the symmetric stretching mode of this shortest Nb=O terminal double bond. Raman bands in the 400–800- $\text{cm}^{-1}$  wavenumber region are assigned to the symmetric and anti-symmetric stretching mode of the Nb-O-Nb linkage, and the associated bending modes appear in the low-wavenumber region (200–300  $\text{cm}^{-1}$ ). Thus, the  $\text{K}_8\text{Nb}_6\text{O}_{19}$ ,  $\text{AlNbO}_4$ , and  $\text{Nb}(\text{HC}_2\text{O}_4)_5$  compounds possess a highly distorted octahedral  $\text{NbO}_6$  structure with Raman bands appearing in the high-wavenumber region, 850–1000  $\text{cm}^{-1}$ , which are characteristic of the symmetric stretching mode of the Nb=O terminal double bond.

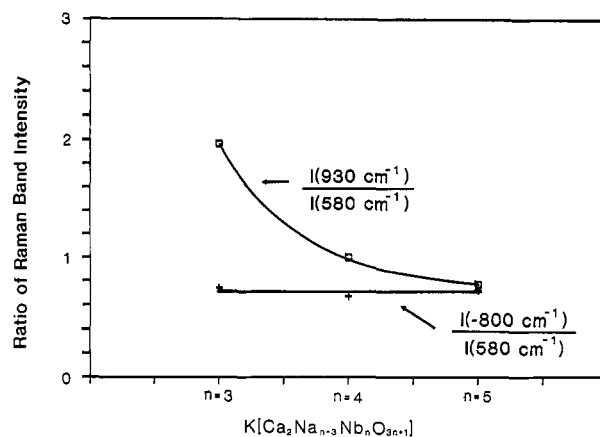


Figure 9. Raman band intensity ratios for the  $\text{KCa}_2\text{Na}_{n-3}\text{Nb}_n\text{O}_{3n+1}$  ( $n = 3-5$ ) layered oxide compounds.

The structure of the  $\text{K}[\text{Ca}_2\text{Na}_{n-3}\text{Nb}_n\text{O}_{3n+1}]$  ( $n = 3-5$ ) layered oxides contains corner-shared  $\text{NbO}_6$  octahedra with a large cation occupying 12-coordinated sites in the center of each cube as found in the perovskite structure.<sup>12</sup> The thickness of each perovskite layer is determined by the number of corner-shared  $\text{NbO}_6$  octahedra connected along the direction perpendicular to the layers ( $n = 3-5$ ). The  $\text{KCa}_2\text{Nb}_3\text{O}_{10}$  structure has been determined by Dion et al.<sup>11</sup> to possess two types of  $\text{NbO}_6$  sites connected to the cations (K and Ca): one is the capping sites between two adjacent layers and the other is the internal sites in the layer.

Raman studies also detect the two types of  $\text{NbO}_6$  sites present in the layered oxide compounds: a highly distorted octahedral structure, Raman band at  $\sim 930$   $\text{cm}^{-1}$ , and a slightly distorted octahedral structure, Raman band at  $\sim 580$   $\text{cm}^{-1}$ . The relative concentrations of the two  $\text{NbO}_6$  octahedra in the layered oxide compounds can be determined by taking the ratio of these Raman bands (the integrated Raman intensity of the bands at  $\sim 930$  and  $\sim 580$   $\text{cm}^{-1}$ ). The Raman  $I(\sim 930 \text{ cm}^{-1})/I(\sim 580 \text{ cm}^{-1})$  ratios for the different layered compounds are shown in Figure 9 and decrease with increasing number of niobium oxide layers. For example, the Raman measurements of the layered oxide  $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ ,  $n = 3$ , has  $I(\sim 930 \text{ cm}^{-1})/I(\sim 580 \text{ cm}^{-1}) = 2$ , which reflects the ratio of the highly distorted octahedral sites to the slightly distorted octahedral sites. This is consistent with the layered oxide structure described by Dion et al.<sup>11</sup> Upon decreasing the number of the niobium oxide layers, the  $I(\sim 930 \text{ cm}^{-1})/I(\sim 580 \text{ cm}^{-1})$  ratio further decreases to 1 for  $\text{K}(\text{Ca}_2\text{Na})\text{Nb}_4\text{O}_{13}$ ,  $n = 4$ , and 0.8 for  $\text{K}(\text{Ca}_2\text{Na}_2)\text{Nb}_5\text{O}_{16}$ ,  $n = 5$ , as expected from the known structures.<sup>12</sup> The quantitative agreement between the Raman ratios and the actual ratios in these layered structures reveals that the Raman cross sections of the slightly distorted and highly distorted  $\text{NbO}_6$  octahedra are essentially the same. The Raman  $I(\sim 800 \text{ cm}^{-1})/I(\sim 580 \text{ cm}^{-1})$  ratios in Figure 9, however, do not change with increasing number of niobium oxide layers. This indicates that the Raman band at  $\sim 800$   $\text{cm}^{-1}$  is associated with the slightly distorted  $\text{NbO}_6$  site band at  $\sim 580$   $\text{cm}^{-1}$  and corresponds to different Nb-O bond lengths. Increasing the number of niobium oxide layers also shifts the band from  $\sim 760$  to  $\sim 840$   $\text{cm}^{-1}$  and eliminates the Raman bands at  $\sim 450$  and  $\sim 375$   $\text{cm}^{-1}$ . These Raman features reflect the different extents of distortions that exist in the layered oxide compounds and are probably due to the different sizes between the Ca and Na cations.

Many of these layered oxide compounds can also undergo an alkali-metal ion exchange reaction with the protons present in aqueous acidic solutions due to their

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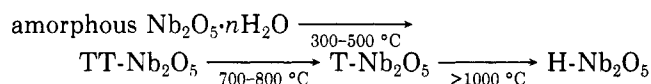
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high ionic conductivity. The potassium cation in the layered oxide  $\text{KCa}_2\text{Nb}_3\text{O}_{10}$  exchanges with the hydrogen proton in an aqueous acidic solution to form the layered oxide  $\text{HCa}_2\text{Nb}_3\text{O}_{10}$ . The layered oxide  $\text{HCa}_2\text{Nb}_3\text{O}_{10}$  possesses a tetragonal unit cell with an interlayer separation 14.38 Å, which is contracted relative to the values of 14.73 Å observed for the layered oxide  $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ .<sup>13</sup> When hydrogen replaces potassium, the interlayer hydrogen stabilizes the terminal oxygen atoms by forming a terminal -OH group interacting with a terminal oxygen in the adjacent layer. The stoichiometry corresponds to one proton for every pair of terminal oxygens from the adjacent layers. The hydrated  $\text{HCa}_2\text{Nb}_3\text{O}_{10}$  compound has a composition  $\text{HCa}_2\text{Nb}_3\text{O}_{10} \cdot 1.5\text{H}_2\text{O}$  with an interlayer separation 16.23 Å. The interlayer hydrogen bonding between the two adjacent terminal oxygens creates some free volume in the  $\text{HCa}_2\text{Nb}_3\text{O}_{10}$  structure to accommodate 1.5 water molecules.<sup>13</sup>

The in situ Raman studies of the layered oxide  $\text{HCa}_2\text{Nb}_3\text{O}_{10}$  indicate that the Nb=O terminal double bond is affected by the adsorbed water since the Raman band at  $\sim 965\text{ cm}^{-1}$  broadens and splits into two bands at  $\sim 980$  and  $\sim 960\text{ cm}^{-1}$  upon dehydration (see Figure 4). The Raman band at  $\sim 840\text{ cm}^{-1}$  is assigned to the Nb=O antisymmetric stretching mode, which is better resolved in the hydrated state. Thus, the in situ Raman studies demonstrate that the water molecules in the layered oxide  $\text{HCa}_2\text{Nb}_3\text{O}_{10}$  structure associate with all the interlayered terminal oxygens to form Nb=O...H bonds. The results are in agreement with the structural studies of Jacobson et al.<sup>13</sup> The in situ Raman studies of the layered oxide  $\text{HCa}_2\text{Nb}_3\text{O}_{10}$  also reveal that hydrogen bonding via water molecule addition results in a decrease in the Nb=O bond order and its corresponding vibrational frequency.

Bulk  $\text{Nb}_2\text{O}_5$  undergoes the following phase transformations during heat treatments:<sup>38-40</sup>



The amorphous  $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  contains slightly distorted  $\text{NbO}_6$ ,  $\text{NbO}_7$ , and  $\text{NbO}_8$  polyhedra.<sup>1</sup> The strong and broad Raman band at  $\sim 650\text{ cm}^{-1}$  is assigned to the symmetric stretching mode of the niobia polyhedra. The broad Raman feature reflects the distribution of the  $\text{NbO}_6$ ,  $\text{NbO}_7$ , and  $\text{NbO}_8$  sites in the structure of the amorphous  $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ . The weak and broad Raman band at  $\sim 900\text{ cm}^{-1}$  is assigned to the symmetric stretching mode of the Nb=O surface sites because of the response of this band to surface dehydration during the in situ Raman studies (see following paragraph). Heat treatment at  $500\text{ }^\circ\text{C}$  for 2 h leads to crystallization into the TT- $\text{Nb}_2\text{O}_5$  phase. The corresponding shift of the Raman band from  $\sim 650$  to  $\sim 690\text{ cm}^{-1}$  is due to the increasing bond order of the niobia polyhedra, and the sharpening of Raman band at  $\sim 690\text{ cm}^{-1}$  is due to the more ordered structure present in the TT- $\text{Nb}_2\text{O}_5$  phase. The TT- $\text{Nb}_2\text{O}_5$  phase contains octahedral and pentagonal bipyramid structures, and the weak Raman band at  $\sim 900\text{ cm}^{-1}$  is due to the small concentration of Nb=O surface sites after the thermal treatment. Additional Raman bands in the low-wavenumber region,  $200\text{--}300\text{ cm}^{-1}$ , are also observed in the TT- $\text{Nb}_2\text{O}_5$  spectrum, which are characteristic of the bending modes of the Nb-O-Nb linkages. Raman features of the T- $\text{Nb}_2\text{O}_5$  ( $800\text{ }^\circ\text{C}$ ) phase are similar to those of the TT- $\text{Nb}_2\text{O}_5$  ( $500\text{ }^\circ\text{C}$ ) phase

(see Figure 6). This indicates that the T- $\text{Nb}_2\text{O}_5$  ( $800\text{ }^\circ\text{C}$ ) phase possesses a structure similar to that of the TT- $\text{Nb}_2\text{O}_5$  ( $500\text{ }^\circ\text{C}$ ) phase and is consistent with Weissman et al.'s conclusions that the TT- $\text{Nb}_2\text{O}_5$  and T- $\text{Nb}_2\text{O}_5$  phases possess nearly identical structures.<sup>4</sup>

The H- $\text{Nb}_2\text{O}_5$  phase contains  $3 \times 4$  and  $3 \times 5$  blocks of corner- or edge-shared octahedral  $\text{NbO}_6$  as well as 1 tetrahedral site per 28 Nb sites. Bhide et al.<sup>41</sup> have assigned the Raman band in the high-wavenumber region,  $900\text{--}1200\text{ cm}^{-1}$ , to the Nb=O terminal bond. Therefore, Raman bands at  $\sim 997$  and  $\sim 900\text{ cm}^{-1}$  for the H- $\text{Nb}_2\text{O}_5$  phase in Figure 6 are characteristic of the symmetric and antisymmetric stretching modes of the Nb=O terminal bond. Blasse<sup>23</sup> studied the  $\text{YNbO}_4$  compound by Raman spectroscopy and determined that the tetrahedral  $\text{NbO}_4$  possesses a major Raman band at  $830\text{ cm}^{-1}$ . McConnell et al.<sup>3</sup> and Iwasawa et al.<sup>42</sup> referred to Blasse's result and determined that the Raman band at  $840\text{ cm}^{-1}$  in H- $\text{Nb}_2\text{O}_5$  is due to the tetrahedral  $\text{NbO}_4$  structure. This assignment is not correct because Blasse did not address that the transition of  $\text{YNbO}_4$  from the octahedral fergusonite to the tetrahedral scheelite depends on temperature.<sup>30</sup> In addition, the Nb-O bond distances of the tetrahedral site in H- $\text{Nb}_2\text{O}_5$  have been determined to be 1.65 and 1.68 Å by Gatehouse et al.<sup>7</sup> The predicted Raman frequency with corresponding Nb-O bond distance of the H- $\text{Nb}_2\text{O}_5$  tetrahedral site appears at  $993\text{ cm}^{-1}$  by using Hardcastle's bond distance/frequency correlation with the overall uncertainty of  $30\text{ cm}^{-1}$ .<sup>43</sup> Thus, the Raman band at  $840\text{ cm}^{-1}$  for H- $\text{Nb}_2\text{O}_5$  can not be assigned to the  $\text{NbO}_4$  tetrahedron. The corner-shared octahedral  $\text{NbO}_6$  in the H- $\text{Nb}_2\text{O}_5$  phase forms a Nb-O-Nb collinear bond with a corresponding Raman band appearing at  $\sim 840\text{ cm}^{-1}$ .<sup>1</sup> Raman bands in the  $500\text{--}800\text{ cm}^{-1}$  region are characteristic of the stretching modes of the slightly distorted octahedral  $\text{NbO}_6$  structures. At the low-temperature treatments ( $<800\text{ }^\circ\text{C}$ ), the structure of niobium oxide possesses the slightly distorted octahedral niobia polyhedra. The structure of the niobium oxide treated at high temperatures, greater than  $1000\text{ }^\circ\text{C}$ , possesses a highly distorted octahedral  $\text{NbO}_6$  structure in addition to the slightly distorted octahedral  $\text{NbO}_6$  structure. Thus, the phase transformations of niobium oxide are strongly dependent on the heat treatments, and this is reflected in the Raman spectra.

During in situ Raman experiment the samples are heated to desorb the adsorbed moisture, and those Raman features that respond to the dehydration treatment are identified as surface functionalities.<sup>44</sup> This process is reversed by reabsorbing water vapor on the surface functionalities. The in situ Raman studies of  $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  (see Figure 7) demonstrate that the broad and weak Raman bands in the  $800\text{--}900\text{ cm}^{-1}$  region shift to higher frequencies due to thermal desorption of the adsorbed moisture. After dehydration of  $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  at  $400\text{ }^\circ\text{C}$  in air for 1 h, two new Raman bands are observed at  $\sim 930$  and  $\sim 980\text{ cm}^{-1}$  which are characteristic of two different Nb=O surface sites. No phase transformations occurred during this thermal treatment since the Raman features of bulk niobium oxide remained the same. The concentration of the Nb=O terminal sites of bulk  $\text{Nb}_2\text{O}_5$  (pretreated at  $500\text{ }^\circ\text{C}$ ) is too small to be observed due to the much lower surface area. Thus, the amorphous  $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  material

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possesses terminal Nb=O sites on the surface, and the number of terminal Nb=O sites can be eliminated by high-temperature calcinations which dramatically decreased the surface area. The in situ Raman studies confirm the presence of the terminal Nb=O surface sites on amorphous  $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  and the assignment of the Raman band at  $\sim 900 \text{ cm}^{-1}$  to the terminal Nb=O surface sites.

### Conclusions

The relationships between niobium oxide structures and their corresponding Raman spectra were systematically studied for various types of niobium oxide compounds. The Raman frequencies strongly depend on the bond order of the niobium oxide structure. A higher niobium-oxygen bond order, corresponding to a shorter bond distance, shifts the Raman frequency to higher wavenumbers. Most of the niobium oxide compounds possess an octahedrally coordinated  $\text{NbO}_6$  structure, slightly or highly distorted. Only a few niobium oxide compounds (such as  $\text{YNbO}_4$ ,  $\text{YbNbO}_4$ ,  $\text{LaNbO}_4$ , and  $\text{SmNbO}_4$ ) can possess a tetrahedrally coordinated  $\text{NbO}_4$  structure that is similar to the scheelite-like structure. For the tetrahedral  $\text{NbO}_4$  struc-

ture, the major Raman frequency appears in the  $790\text{--}830\text{-cm}^{-1}$  region. For the slightly distorted octahedral  $\text{NbO}_6$  structure, the major Raman frequencies appear in the  $500\text{--}700\text{-cm}^{-1}$  wavenumber region. For the highly distorted octahedral  $\text{NbO}_6$  structure, the Raman frequency shifts from the  $500\text{--}700\text{-cm}^{-1}$  to the  $850\text{--}1000\text{-cm}^{-1}$  region. Both slightly distorted and highly distorted octahedral  $\text{NbO}_6$  sites coexist in the  $\text{KCa}_2\text{Na}_{n-3}\text{Nb}_n\text{O}_{3n+1}$ ,  $n = 3\text{--}5$ , layered compounds. The distortions in the niobium oxide compounds are caused by the formation of corner- or edge-shared  $\text{NbO}_6$  octahedra.

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**Registry No.**  $\text{KNbO}_3$ , 12030-85-2;  $\text{NaNbO}_3$ , 12034-09-2;  $\text{LiNbO}_3$ , 12031-63-9;  $\text{K}_8\text{Nb}_6\text{O}_{19}$ , 12031-11-7;  $\text{AlNbO}_4$ , 12258-25-2;  $\text{Nb}(\text{CH}_2\text{O}_4)_5$ , 12404-95-4;  $\text{K}(\text{Ca}_2\text{Na}_2)\text{Nb}_5\text{O}_{16}$ , 98820-43-0;  $\text{K}(\text{Ca}_2\text{Na})\text{Nb}_4\text{O}_{13}$ , 98820-40-7;  $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ , 80487-87-2;  $\text{HCa}_2\text{Nb}_3\text{O}_{10}$ , 98820-36-1;  $\text{Nb}_2\text{O}_5$ , 1313-96-8;  $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ , 12326-08-8;  $\text{YbNbO}_4$ , 12034-62-7.

## Phase-Transfer Palladium(0)-Catalyzed Polymerization Reactions. 6. Synthesis and Thermotropic Behavior of Mono- and Difluorinated 1,2-Bis(4-*n*-alkoxyphenyl)acetylene Monomers<sup>†</sup>

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Symmetrically difluorinated 1,2-bis(3-fluoro-4-*n*-alkoxyphenyl)acetylene ( $n = 4\text{--}12$ ) and asymmetric, monofluorinated 1-(3-fluoro-4-*n*-alkoxyphenyl)-2-(4-*n*-alkoxyphenyl)acetylene ( $n = 5\text{--}12$ ) monomers were prepared by a one-pot, phase-transfer Pd(0)/Cu(I)-catalyzed three-step coupling of the appropriate aryl halides with 2-methyl-3-butyn-2-ol. All odd members of the 1,2-bis(3-fluoro-4-*n*-alkoxyphenyl)acetylene series are crystalline with a virtual nematic mesophase. All even members of the series present monotropic nematic mesophases. The thermotropic behavior of the 1-(3-fluoro-4-*n*-alkoxyphenyl)-2-(4-*n*-alkoxyphenyl)acetylenes changes continuously with *n*. The  $n = 5$  derivative is crystalline. The  $n = 6\text{--}10$  derivatives each have an enantiotropic nematic mesophase. In addition, the  $n = 7, 8$  derivatives exhibit an enantiotropic smectic mesophase, and the  $n = 9, 10$  derivatives exhibit monotropic smectic C mesophases. Both the nematic and smectic C mesophases of the  $n = 11, 12$  derivatives are monotropic.

### Introduction

In a recent publication,<sup>1</sup> we described a one pot, solid-liquid phase-transfer Pd(0)/Cu(I)-catalyzed synthesis of 1,2-bis(4-alkoxyaryl)acetylenes from aryl halides deactivated by alkoxy substituents. The three-step, one-pot synthesis outlined in Scheme I was adapted from Carpita<sup>2</sup> et al.'s liquid-liquid phase-transfer catalyzed synthesis of diheteroarylacetylenes. In the first step, an aromatic halide is coupled with a monoprotected acetylene. The resulting carbinol derivative is deprotected in the second step with

formation of an aryl acetylene, which is then coupled with a second aryl halide in the final step. In this phase-transfer catalyzed (PTC), one-pot procedure, only the final diarylacetylene product is isolated.

The subsequent papers in this series described the thermotropic behavior of both symmetrically and asymmetrically substituted 1,2-bis(4-alkoxyaryl)acetylene monomers.<sup>3-5</sup> The linear 1,2-bis(4-*n*-alkoxyphenyl)acetylenes

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