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Synthesis and Structural Studies of Microporous Titanium−Niobium−Silicates with the Structure of Nenadkevichite

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A series of synthetic microporous analogues of the mineral nenadkevichite, with Ti/Nb molar ratios ranging from 0.8 to 17.1 and a purely titaneous sample, have been prepared. The microporous titanosilicate ETS-4 has been found to be a precursor in the synthesis of synthetic nenadkevichite. The structure of nenadkevichite materials has been extensively characterized by scanning electron microscopy, powder X-ray diffraction, Raman spectroscopy, diffuse-reflectance ultraviolet spectroscopy (DR-UV), and ^{23}Na, ^{29}Si, and ^{93}Nb high-resolution solid-state NMR. In accord with the published structure for the mineral nenadkevichite, DR-UV and ^{93}Nb solid-state NMR suggest that titanium and niobium are in distorted octahedral coordination. Raman spectroscopy clearly shows the framework substitution of titanium for niobium. In addition, due to stronger dipolar interactions, the replacement of ^{47}Ti and ^{49}Ti (diluted quadrupolar nuclei) by ^{93}Nb (abundant quadrupolar nucleus) results in a significant decrease in the ^{29}Si spin−spin (T_2) NMR relaxation times. The ^{29}Si NMR spectra are strongly dependent on the cations present and on the state of hydration of the nenadkevichite materials.

Introduction

Recently, the synthesis and characterization of novel zeolite-type materials containing atoms in 6-fold coordination, particularly microporous titanosilicates, has attracted much interest. ETS-10 is one of the most interesting porous titanosilicates; its structure has been solved, and it contains Ti^{4+} corner-sharing octahedra and silicon corner-sharing tetrahedra.[1,2] The structure of ETS-10 may be described in terms of an intergrowth of two end member polymorphs, termed A and B, both of which consist of a three-dimensional 12-membered ring structure. Polymorph A belongs to a chiral space group and, like zeolite β, has a spiral channel. Reports on the isomorphous substitution of silicon by aluminum and gallium in ETS-10 have also appeared.[3,4] In a previous communication[5] we have described briefly the synthesis and structural characterization of synthetic analogues of nenadkevichite, a microporous titanium−niobium−silicate mineral, and here we expound on these studies. Nenadkevichite from Lovozero (Russia), first described by Kouzmenko and Kazakova, has the composition $(Na,Ca)(Nb,Ti)Si_2O_7 \cdot 2H_2O$.[6] Nenadkevichite from Saint-Hilaire, Quebec (Canada), crystallizes in space group *Pbam*: $a = 7.41$, $b = 14.20$, and $c = 7.15$ Å. Its structure consists of square rings of silica tetrahedra Si_4O_{12} in the (100) plane joined together by chains of NbO_6 octahedra in the [100] direction (see Figure 1).[6] The pores accommodate Na in two partially (0.53 and 0.54) occupied sites and H_2O in two fully occupied sites. Other minerals with a similar structure contain progressively more Ti^{4+} proxying for Nb^{5+} to the mineral labuntsovite, which is essentially $(Na,K,Ba)_2Ti_2(O,OH)_2Si_4O_{12} \cdot 3H_2O$.[7,8]

Experimental Section

Synthesis. We have prepared synthetic analogues of nenadkevichite with Ti/Nb molar ratios of (as ascertained by energy dispersive absorption of X-rays, EDAX) 0.8, 2.0, 4.1, 12.3, and 17.1. We have also synthesized a purely titaneous sample.

Synthesis of Nenadkevichite with Ti/Nb = 4.1. An alkaline solution was made by mixing 10.06 g of sodium silicate (Na_2O 8% *m/m*, SiO_2 27% *m/m*), 15.05 g of H_2O, 2.3 g of NaOH, 0.96 g of KF, 0.38 g of KCl, 0.46 g of NaCl, 4.63 g of $TiCl_3$ (15% *m/m* solution of $TiCl_3$ in 10% *m/m* HCl), and 0.15 g of Nb_2O_5. A 0.10 g seed of nenadkevichite was added to the resulting gel. This gel, with a composition 7.33:2.44:10.0:0.12: 184 $Na_2O/K_2O/SiO_2/TiO_2/Nb_2O_5/H_2O$, was autoclaved under autogeneous pressure for 5 days at 230 °C. The resulting product was cooled down to room temperature, filtered, washed with distilled water, and dried overnight at 120 °C. Thermogravimetric analysis (TGA) revealed a weight loss from 50 to 550 °C of 10 ± 1% for samples with different niobium contents.

Techniques. ^{23}Na, ^{29}Si, and ^{93}Nb solid-state NMR spectra were recorded at 105.81, 79.49, and 97.84 MHz (9.4 T) on a Bruker MSL 400P spectrometer. ^{23}Na spectra were measured using short and powerful radiofrequency pulses (0.6 μs, equivalent to 15° pulse angle), a spinning rate of 15 kHz, and a recycle delay of 2 s. Chemical shifts are quoted in ppm from 1 M NaCl. ^{29}Si spectra were recorded with 40° pulses, spinning rates of 5.0−5.5 kHz, and a 35 s recycle delays. To measure spin−spin relaxation times, the Carr−Purcell−Meiboom−Gill (CPMG) sequence ($90_x−\tau−180_y−$acquire) was used. Chemical shifts are quoted in ppm from TMS. ^{93}Nb spectra were recorded with 0.6 μs (6°) pulses, spinning rates of 10.0−16.0 kHz, and a 0.5 s recycle delay. Chemical shifts are quoted in ppm from solid Nb_2O_5. Powder X-ray diffraction (XRD) data were collected on a Rigaku diffractometer using Cu Kα radiation filtered by Ni. Scanning electron microscope (SEM) images were recorded on a Hitachi S-4100 microscope. Raman spectra were measured at room temperature with a Renishaw imaging microscope 2000, using a 25 mW Spectra Physics 127 HeNe excitation laser (632.8 nm), a resolution of 1 cm^{-1}, and an air-cooled CCD detector. Diffuse-reflectance ultraviolet (DR-UV)

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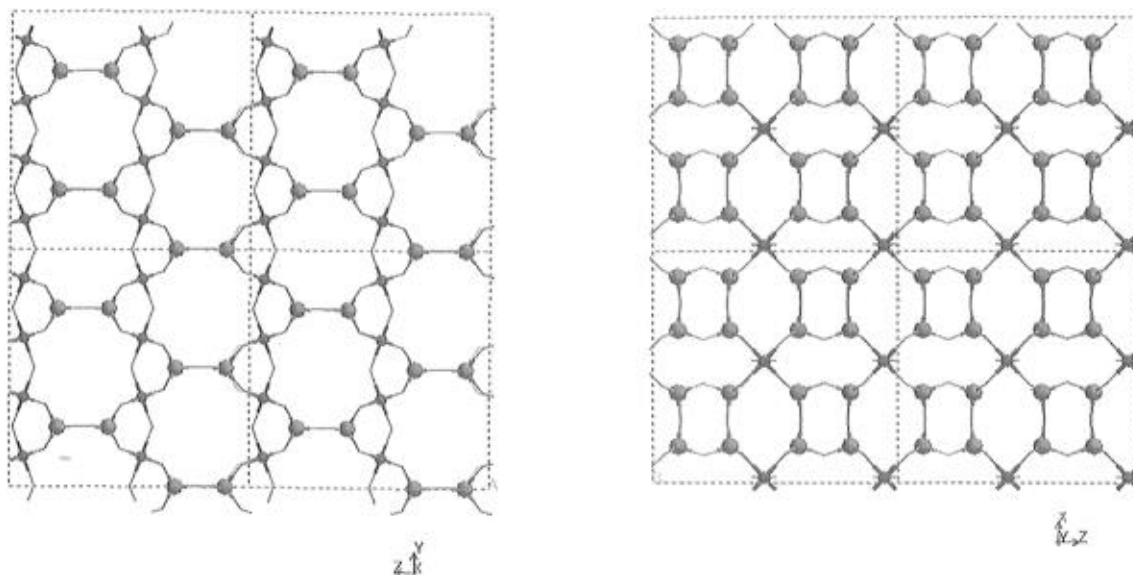⊗ Abstract published in *Advance ACS Abstracts,* August 15, 1996.

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Figure 1. Nenadkevichite structure: (100) (left) and (001) (right) projections. Large and small solid circles denote Si and Ti atoms.
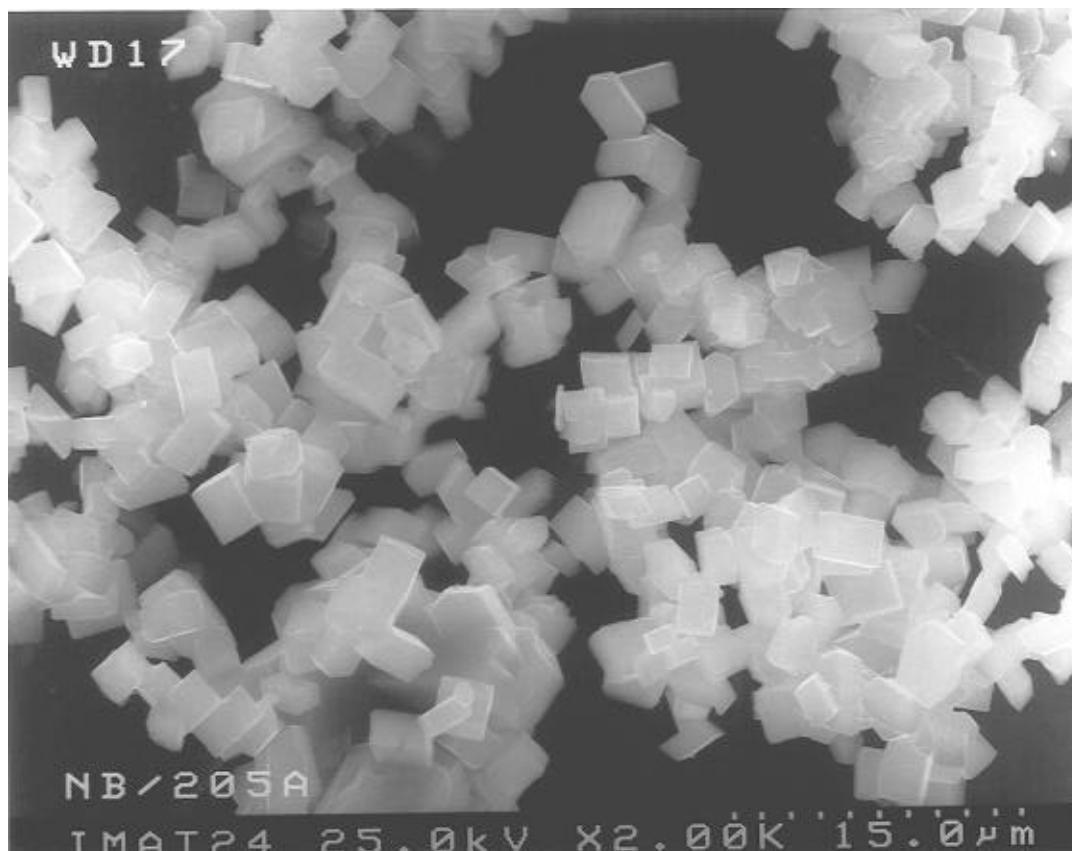

Figure 2. Typical SEM images of synthetic nenadkevichite.

spectra were recorded on a Shimadzu 3101PC spectrometer using $BaSO_4$ as the reference material. Since the samples with Nb/Ti ratios of 12.3 and 17.1 give similar XRD, NMR, Raman, and DR-UV spectra, we shall only refer to the former.

Results and Discussion

Study of the Synthesis. We have carried out a detailed study of the synthesis of a nenadkevichite sample with *final* Ti/Nb = 1.2 (see Figure 2). The ^{29}Si MAS NMR spectra (see Figure 3) clearly show that different phases form as a function of the pH (measured after a 1:100 dilution with water) of the initial gel. ETS-10 (with no framework niobium) crystallizes at a relatively

low pH (9.0−11.0). The microporous titanosilicate ETS-4[9] is stable between pH 11.0 and *ca.* 11.6, while nenadkevichite analogues form in the pH range of 11.6−12.2. Above pH 12.4 an, as yet, unidentified titanosilicate forms. These NMR observations are supported by powder XRD data (not shown). In the course of the synthesis (the pH of the starting gel is 11.8), powder XRD and ^{29}Si solid-state NMR (not shown) indicate that ETS-4 forms after 2 h. Raman spectroscopy of a small group of single crystals suggests that the precursor ETS-4 contains some niobium (see discussion below); the Ti/Nb molar ratio determined by careful EDAX analysis is 13.3. The same sample also contains niobium oxide and a small amount of
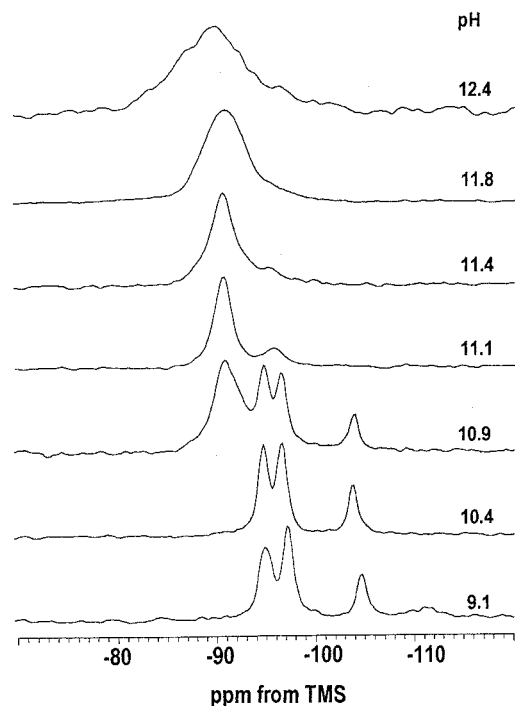
Figure 3. ^{29}Si solid-state MAS NMR spectra of the products of the synthesis of nenadkevichite obtained from starting gels with pH values indicated.
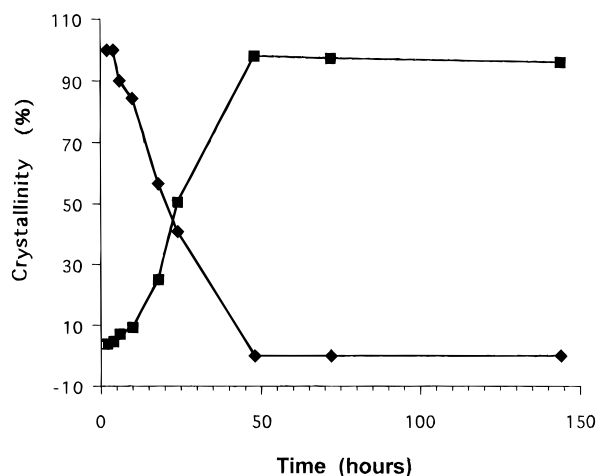

Figure 4. Powder XRD crystallinity curves for ETS-4 (diamonds) and synthetic nenadkevichite (squares). The individual points were calculated by normalizing the sum of the intensities of the lines at 7.1, 16.4, and 19.8 2θ (ETS-4) and 13.6, 17.8, and 27.7 2θ (nenadkevichite) to the corresponding intensity sum of a sample reacted for 2 h (ETS-4) and 5 days (nenadkevichite).

synthetic nenadkevichite with Ti/Nb = 9.6, which is far poorer in Nb than the final synthesis product (Ti/Nb = 1.2). Consider the crystallinity curves depicted in Figure 4. Between 2 and *ca.* 50 h the synthesis materials are increasingly poorer in ETS-4 and richer in synthetic nenadkevichite. After 50 h of synthesis, and up to 15 days, only the latter is present. ETS-4 appears to be a precursor in the synthesis of nenadkevichite materials. Since the dissolution of Nb_2O_5 is relatively slow, the formation of ETS-4 may prevent the early segregation of silica and titania. Relatively large amounts of niobium seem to be incorporated only when ETS-4 transforms to synthetic nenadkevichite (via a solid-state reaction or a solution-mediated process).

Structural Studies. *Powder X-ray Diffraction.* The powder XRD patterns of the titanium−niobium−silicate materials prepared (Figure 5) are characteristic of nenadkevichite (see Joint Committee on Powder Diffraction Studies cards 8-105,
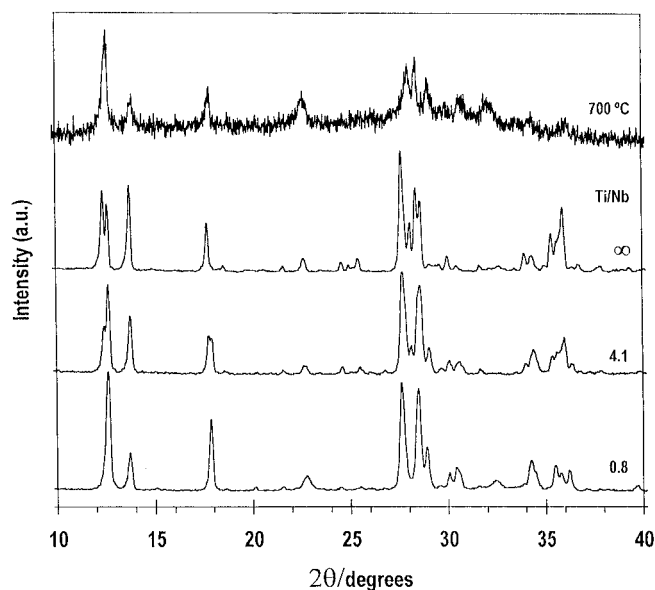

Figure 5. Selected powder XRD patterns of synthetic nenadkevichite materials. The Ti/Nb molar ratios are indicated. The pattern on top (Ti/Nb = 0.8) has been recorded *in situ* at 700 °C. Notice the relatively poor crystallinity of this material.
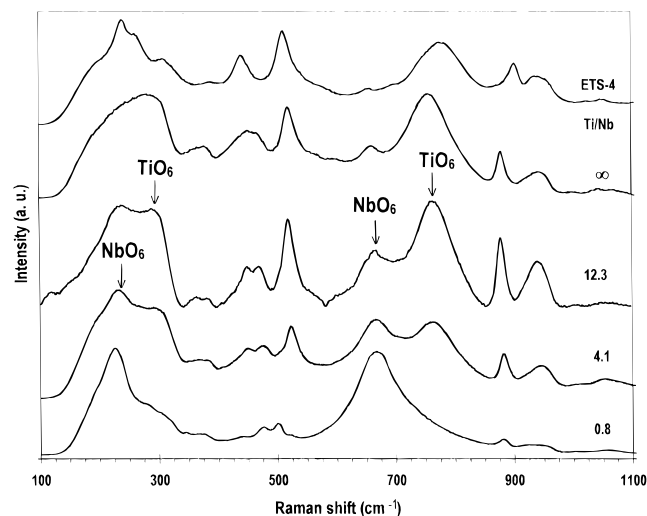

Figure 6. Selected Raman spectra of synthetic nenadkevichite materials measured at room temperature. The Ti/Nb molar ratios are indicated. For comparison, the spectrum of ETS-4 is also depicted.

37-484, and 25-1189).[7,8] For Ti/Nb > 4.0, a splitting of the lines at 12.7° 2θ and 27−29° 2θ is observed. Interestingly, the XRD pattern of the sample containing no niobium is characteristic of nenadkevichite rather than labuntsovite. An *in situ* variable temperature powder XRD study of a sample with Ti/Nb = 0.8 (see selected pattern in Figure 5) shows that the crystallinity is retained up to about 700 °C, although it decreases significantly above 600 °C.

Raman Spectroscopy. Raman spectra provide perhaps the best evidence for the isomorphous substitution of Ti^{4+} for Nb^{5+} in the framework of synthetic nenadkevichite. The Raman spectra of Ti/Nb = 0.8 nenadkevichite (see Figure 6) displays two main bands at 668 and 226 cm^{-1}, which we attribute to NbO_6 octahedra. With increasing Ti content, the Raman intensity of these bands decreases (particularly of the former) while simultaneously two other strong bands grow at *ca.* 764 and 290 cm^{-1}. We assign these bands to TiO_6 octahedra. The bands at 940, 878, and 520 cm^{-1} also increase its intensity. Niobium−silicate glasses and several crystalline solids give bands at 600−800 cm^{-1}, which have been assigned to NbO_6

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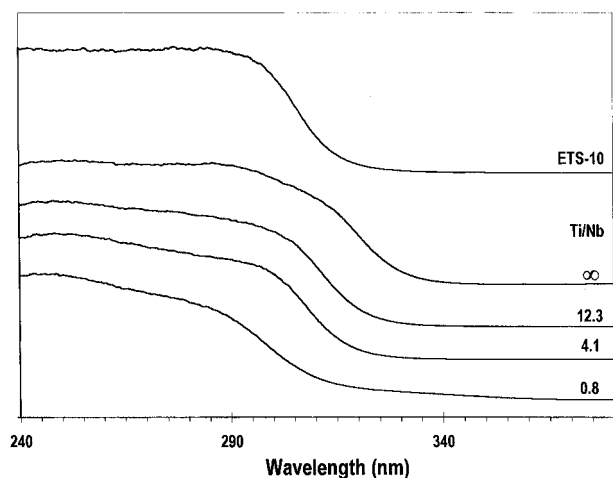*J. Phys. Chem., Vol. 100, No. 36, 1996* **14981**

Figure 7. DR-UV spectra of nenadkevichite materials The Ti/Nb molar ratios are indicated. For comparison, the spectrum of ETS-10 is also depicted.
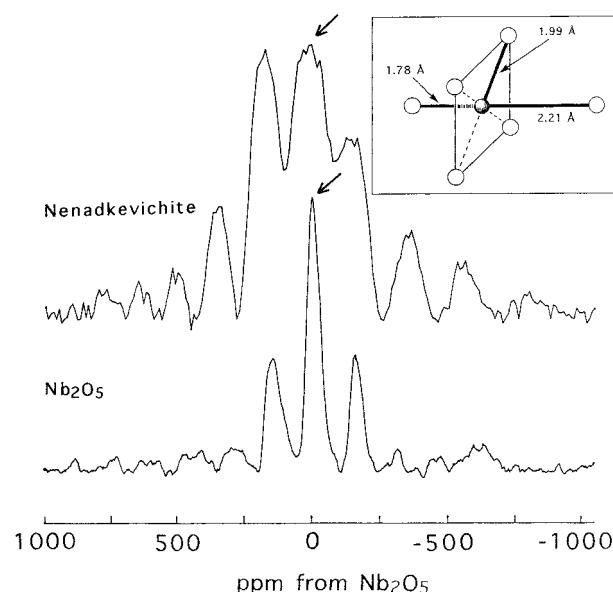

Figure 8. Typical ^{93}Nb MAS NMR spectra of synthetic nenadkevichite (Ti/Nb = 2.0). For comparison, the spectrum of Nb_2O_5 is also depicted. The arrows depict the central line (the other peaks are spinning sidebands). The inset shows the local environment of Ti and Nb in the mineral nenadkevichite.

octahedra with *no* nonbridging oxygens (see ref 10 and references therein). Bands seen at $230-280$ cm^{-1} are also probably associated with NbO_6 octahedra.[10] On the other hand, titanosilicate glass bands at $770-780$ cm^{-1} have been assigned to the Si−O−Ti vibration of Ti in octahedral coordination and the bands at 710 cm^{-1} may be due to the Ti−O−Ti vibration in octahedral coordination.[11] Bands in this spectral range may, in addition, contain a contribution from SiO_4 deformations. The bands at $274-310$ cm^{-1} have been assigned to O−Ti−O rocking.[11] ETS-10 (not shown) and ETS-4 contain octahedral Ti^{4+} and give strong bands at 720 and 775 cm^{-1} and several bands centered at *ca.* 310 and 240 cm^{-1}, respectively. Very recently, Mihailova *et al.*[12] published Raman spectra of ETS-4 and ETS-10 which differ somewhat from the spectra given by the materials prepared in our laboratory. Although we do not wish to discuss here in more detail the vibrational spectra of ETS materials, it may be of interest to recall that Mihailova *et al.* assigned the bands in the range of $400-800$ cm^{-1} to (predominantly) the internal modes of the Ti polyhedra while the low-frequency bands (<400 cm^{-1}) were ascribed to Si−O−Ti interactions.

The products of the synthesis of nenadkevichite analogues were studied by Raman spectroscopy; the sample reacted for 2 h (see discussion above) is of particular interest. It contains ETS-4, niobium oxide, and a rather small amount of synthetic nenadkevichite. Since the Raman spectra of the bulk material is dominated by the niobium oxide bands, we have recorded spectra of a few ETS-4 crystals using the microscope facility of our spectrometer. These spectra (not shown) are very similar to the spectrum of bulk ETS-4 shown in Figure 6 but they also display a strong band at 668 cm^{-1}. Since EDAX analysis of the same sample also indicates that single crystals of ETS-4 contain Nb, we are convinced that the precursor ETS-4 indeed contains framework niobium. In order to clearly establish that ETS-4 may be prepared with niobium in the framework, we are at present engaged in detailed synthetic studies.

Diffuse-Reflectance Ultraviolet Spectroscopy. DR-UV spectroscopy has been used extensively to probe the insertion of Ti atoms into tetrahedral framework sites of TS materials (see ref 13 and references therein). ETS-10 contains hexacoordinated Ti atoms and hence is a good DR-UV reference compound for the study of nenadkevichite materials. The UV absorption threshold of ETS-10 (see Figure 7) is shifted about 30 nm to a higher wavelength relative to those of TS-1 and Ti-β, zeolitic materials containing 4-fold Ti.[14] The spectra displayed by nenadkevichite materials are similar (though not identical) to

those of ETS-10, confirming that titanium is hexacoordinated. A small shift of the UV absorption edge to lower wavelength is observed when the samples become richer in niobium. Nenadkevichite materials and Nb_2O_5 give rather different spectra, thus indicating that our samples are essentially free from any niobium oxide impurity.

^{93}Nb, ^{29}Si, and ^{23}Na Solid-State NMR. The ^{93}Nb MAS NMR spectra (see Figure 8) of all nenadkevichite materials display a single and broad resonance centered at *ca.* 0 ppm from Nb_2O_5, consistent with the presence of hexacoordinated niobium. The MAS sideband pattern associated with this resonance is complex even when the sample is spun at 16 kHz, indicating that the local niobium environment in nenadkevichite is more distorted than in Nb_2O_5. It is interesting to examine in detail the local environment of Nb(IV) in the mineral nenadkevichite (see inset in Figure 8).[6] The coordination octahedron is only slightly distorted: the O−O distances are all between 2.773 and 2.839 Å. However, Nb is not in the center of the octahedron, rather it is shifted toward one of the corners. In this way, along each one-dimensional niobium−oxygen (or titanium−oxygen) chain (−O−Nb−O−Nb−), long (2.21 Å) and short (1.78 Å) Nb−O bonds alternate. A similar situation occurs in ETS-10.[15] These distorted Ti−O and Nb−O environments are not unprecedented in other inorganic solids. The nonlinear optical material KTiO-(PO_4) and other related titanyl phosphate chain compounds are shown to possess a similar Ti−O environment according to single-crystal structural analysis.[16,17] ^{93}Nb is a spin $^9/_2$ nucleus with a relatively large quadrupole moment (-0.22×10^{28} m^{-2}). Only when the local coordination polyhedra are not very distorted is it possible to record central ($m = \pm^1/_2 \leftrightarrow m = \pm^1/_2$) transition lines. Any small deviation from cubic symmetry will generate electric field gradients at the nucleus site which will broaden the lines, making detection sometimes impossible. The spectrum of nenadkevichite materials is consistent with the small distortion of the coordination octahedra found in mineral samples.

The ^{29}Si solid-state MAS NMR spectra (see Figure 9) of nenadkevichite materials contain a main peak at *ca.* -90.8 ppm. No differences have been found between these spectra and the ^{1}H−^{29}Si cross-polarization MAS spectra (not shown). Previ-
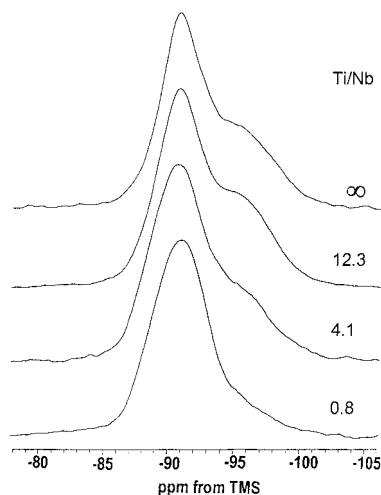
Figure 9. ^{29}Si solid-state MAS NMR spectra of nenadkevichite materials. The Ti/Nb molar ratios are indicated.
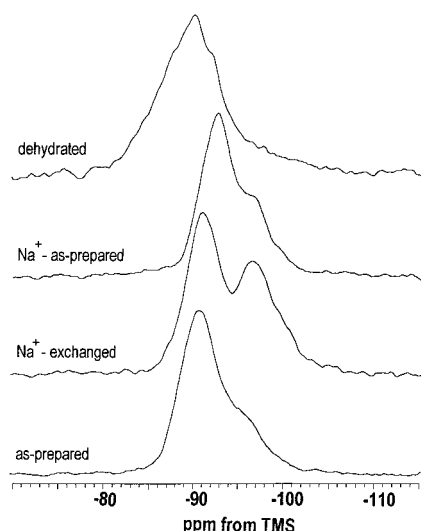

Figure 10. ^{29}Si solid-state MAS NMR spectra of as-prepared (containing Na$^+$ *and* K$^+$; Ti/Nb = 4.1), Na$^+$-exchanged, as-prepared (containing *only* Na$^+$; Ti/Nb = 4.7), and (Na$^+$, K$^+$, Ti/Nb = 4.1) dehydrated nenadkevichite materials.

ously, we have shown that for microporous titanosilicates this isotropic chemical shift is characteristic of Si(2Si, 2Ti) environments (Si bonded via oxygen atoms to 2 Si and 2 Nb atoms).[2] With increasing titanium content this resonance narrows, and a second peak grows at about −96 ppm. Since the published structure of the mineral nenadkevichite calls for the presence of a single Si site of the type Si[2Si, 2Nb(Ti)], the −96 ppm resonance may not arise due to the isomorphous substitution of Ti for Nb. Although the detailed assignment of this resonance is not entirely clear at present, we have found that its intensity is strongly dependent on the cations present. For example, Figure 10 shows that upon Na$^+$ ion exchange the sample with Ti/Nb = 4.1 gives a −96 ppm resonance much stronger than that of the peak seen in the spectrum of the as-prepared sample. In addition, we have prepared a sample (Ti/Nb = 4.7) containing only sodium ions in the parent gel. Again, this sample gives a strong peak around −97 ppm. The main Si[2Si, 2Nb(Ti)] resonance is somewhat shifted (from −90.8 to −92.8 ppm) relative to those of the samples prepared with Na$^+$ and K$^+$. On the other hand, the ^{29}Si NMR spectra are also sensitive to the state of hydration of the samples. Figure 10 clearly shows that upon dehydration the sample (Ti/Nb = 4.1) gives a broad signal shifted to −89.8 ppm; the −96 ppm peak is not observed. It is well-known that the nature and distribution of the exchangeable
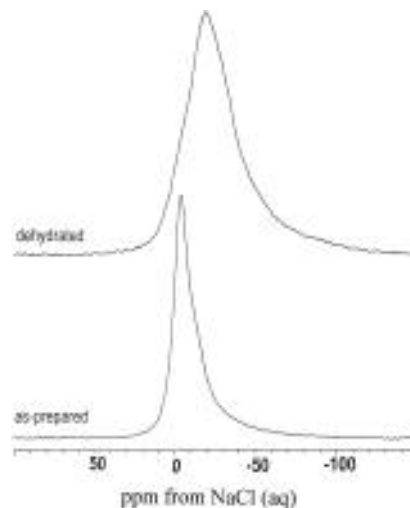

Figure 11. ^{23}Na solid-state MAS NMR spectra of as-prepared (Na$^+$, K$^+$) and dehydrated nenadkevichite materials (Ti/Nb = 4.1).

cations have a significant influence on the ^{29}Si chemical shifts of a given zeolite framework. In zeolites, cation exchange may cause maximum shift differences of 5−6 ppm for all types of Si(nAl) units, comparable to the shift effect due to Al substitution in a given Si(nAl) environment.[18] In dehydrated zeolites, the cations are in general more localized than those in hydrated samples and important changes are observed in the ^{29}Si NMR spectra. In particular, the resonances may be broadened for example by residual ^{23}Na−^{29}Si dipolar interactions not completely averaged out by MAS. In hydrated samples, the rapid site exchange of cations efficiently removes this residual broadening.[18]

It has been reported previously that the spin−spin, T_2, relaxation times of ^{29}Si in microporous titanosilicates are very sensitive (*i.e.*, they decrease significantly) to substitution of framework Si by a quadrupolar nucleus such as ^{27}Al ($I = \frac{5}{2}$).[19] The case of nenadkevichite materials is particularly interesting. The NMR active nuclei ^{47}Ti ($I = \frac{5}{2}$) and ^{49}Ti ($I = \frac{7}{2}$) are relatively diluted (7.28 and 5.51%); they are substitued by ^{93}Nb ($I = \frac{9}{2}$) a 100% abundant nucleus. We have decided to investigate whether the ^{29}Si spin−spin relaxation times are sensitive to such substitution. The T_2 times (MAS 4.5 kHz) for purely titanous and niobium-enriched (Ti/Nb = 0.8) nenadkevichite samples were found to be significantly different, 5.9 ± 0.5 ms (−90.8 and −96 ppm resonances) and 4.1 ± 0.4 ms, respectively. This indicates that Nb replaces Ti in the framework of nenadkevichite materials.

Typical ^{23}Na MAS NMR spectra of nenadkevichite materials (Ti/Nb = 4.1) with different degrees of hydration are shown in Figure 11. The hydrated sample gives a peak at −2.4 ppm with a shoulder at *ca.* −15 ppm, while the dehydrated materials display a broad peak at −17 ppm. The presence of two resonances in the spectra of the hydrated samples is expected, since the structure of the mineral nenadkevichite contains two types of sodium ions. The relative sharpness of the lines given by the hydrated samples may be due to the motional averaging of the quadrupole coupling. On the other hand, the broadening of the ^{23}Na resonance upon dehydration may indicate that the bare Na$^+$ ions produced are located in less symmetric environments than the hydrated sodium ions, Na(H$_2$O)$_n$$^+$.[18]

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