Novel microporous titanium–niobium–silicates with the structure of nenadkevichite

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A series of synthetic microporous analogues of the mineral nenadkevichite are prepared; Raman spectroscopy shows the isomorphous substitution of titanium for niobium in octahedral framework sites.

We have been interested in the synthesis and characterization of novel zeolite-type materials containing atoms in six-fold coordination, particularly microporous titanosilicates. Recently, we have solved the structure of the microporous titanosilicate ETS-10.[1,2] In ETS-10 the Ti^{4+} are corner-sharing octahedra and the Si are corner-sharing tetrahedra. 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. We have also reported on the isomorphous substitution of silicon by aluminium and gallium in ETS-10.[3,4] Here we report the synthesis and structural characterization of synthetic analogues of nenadkevichite a microporous titanium–niobium–silicate mineral. Nenadkevichite from Lovozero (Russia), first described by Kouzmenko and Kazakova, has the composition $(Na,Ca)(Nb,Ti)Si_2O_7{\cdot}2H_2O$.[5] 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 (Fig. 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 $(Na,K,Ba)2Ti_2(O,OH)$-$2Si_4O_{12}{\cdot}3H_2O$.[6,7]

We have prepared synthetic analogues of nenadkevichite with Ti : Nb molar ratios of 0.8, 2.0, 4.1 and 12.3 : 1.† We have also synthesized a purely titanous sample. These materials display powder X-ray diffraction (XRD) patterns (Fig. 2) which are characteristic of nenadkevichite (see JCPDS cards 8-105, 37-484 and 25-1189).[6,7] For Ti : Nb > 4.0 a splitting of the lines at 2θ 12.7 and 27–29 ° is observed. Interestingly, the XRD pattern of the sample containing no niobium is characteristic of nenadkevichite rather than labuntsovite. The ^{29}Si solid-state MAS NMR spectra (not shown) of nenadkevichite materials contain a main peak at δ *ca.* −90.8 confirming the presence of Si(2Si,2Ti) environments.[2] With increasing titanium content a second fainter peak grows at about δ −96. At present, the assignment of this resonance is not clear, although we have observed that it becomes much stronger upon Na^+-ion exchange. The ^{93}Nb MAS NMR spectra (not shown) display a single resonance at δ *ca.* 0 from Nb_2O_5 consistent with the presence of six-coordinate niobium. The sideband MAS pattern associated with this resonance indicates that the local niobium environment in nenadkevichite is more distorted than in Nb_2O_5. The UV diffuse reflectance spectra of nenadkevichite materials and ETS-10 (not shown) are similar, hence confirming that titanium is in an octahedral environment. Raman spectroscopy provides 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 : 1 synthetic nenadkevichite (Fig. 3) displays two main bands at 668 and 226 cm^{-1} which we attribute to NbO_6 octahedra. With

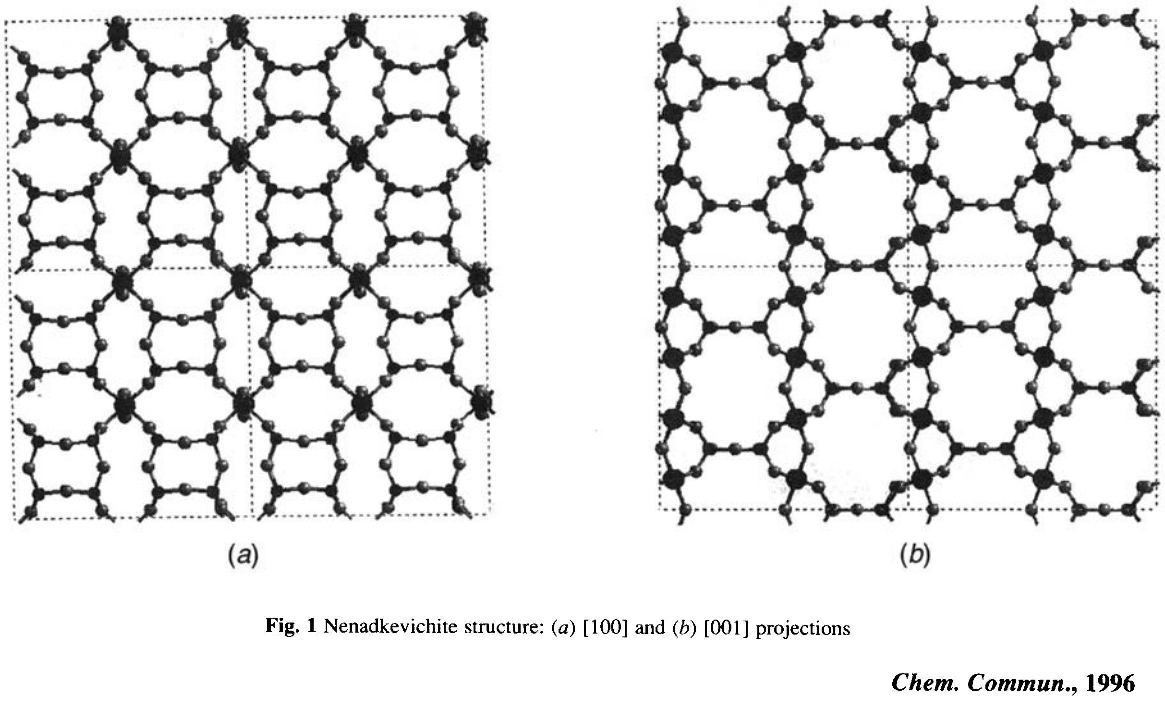

Fig. 1 Nenadkevichite structure: (*a*) [100] and (*b*) [001] projections

increasing Ti content the Raman contribution of these bands decreases dramatically 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 in intensity. Niobium–silicate glasses and several crystalline solids give bands at 600–800 cm^{-1}, which have been assigned to NbO_6 octahedra with *no* non-bridging oxygens (see ref. 8 and references therein). Bands seen at 230–280 cm^{-1} are also probably associated with NbO_6 octahedra.[8] On the other hand, titanosilicate glass bands at 770–780 cm^{-1} have been assigned to the Si–O–T vibration of Ti in octahedral coordination, while bands at 710 cm^{-1} may be due to the Ti–O–Ti vibration in octahedral coordination.[9] Bands in this spectral range may, in addition, contain a contribution from SiO_4 deformations. Bands at 274–310 cm^{-1} have been assigned to O–Ti–O rocking.[9] ETS-10 and ETS-4 contain octahedral Ti^{4+} and give strong bands at 720 and 775 cm^{-1} and several bands centred at *ca.* 310 and 240 cm^{-1} (not shown). In conclusion, Raman spectroscopy clearly shows that octahedral Ni^{5+} is substituted by octahedral Ti^{4+} in the framework of synthetic nenadkevichite.

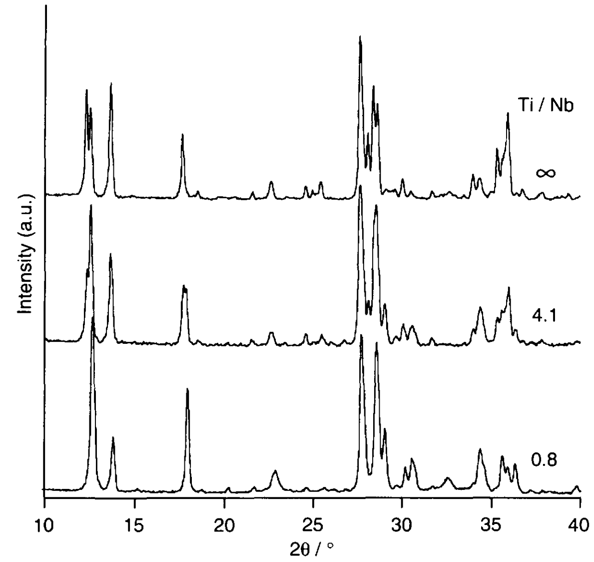

Fig. 2 Selected powder XRD patterns of synthetic nenadkevichite materials. The Ti : Nb molar ratios are indicated.

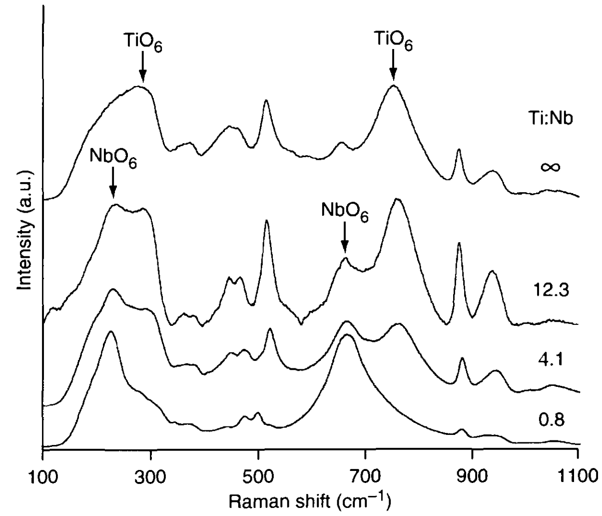

Fig. 3 Selected Stokes shifted Raman spectra of synthetic nenadkevichite materials, measured at room temperature, at 1 cm^{-1} resolution, using a Renishaw Raman imaging microscope model 2000 with a short focal length spectrometer and fitted with a Spectra Physics 127 HeNe laser for excitation at 632.8 nm (25 mW power at the source). The Ti : Nb molar ratios are indicated.

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Footnote

† Synthesis of nenadkevichite with Ti : Nb = 4.1. An alkaline solution was made by mixing 10.06 g sodium silicate (Na_2O 8% *m/m*, SiO_2 27% *m/m*), 15.05 g H_2O, 2.3 g NaOH, 0.96 g KF, 0.38 g KCl, 0.46 g NaCl, 4.63 g $TiCl_3$ (15% *m/m* solution of $TiCl_3$ in 10% *m/m* HCl) and 0.15 g Nb_2O_5. 0.10 g seed of nenadkevichite was added to the resulting gel. This gel, with a composition 7.33 Na_2O : 2.4 K_2O : 10.0 SiO_2 : TiO_2 : 0.12 Nb_2O_5 : 184 H_2O, was autoclaved under autogenous pressure for 7 days at 230 °C. The resulting product was cooled to room temperature, filtered and washed with distilled water and dried overnight at 120 °C. TGA revealed a mass loss from 50 to 550 °C of 9–11%.

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