

Synthesis of a new titanosite: an analogue of the mineral penkviksite

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A new titanosite which is a structural analogue of the mineral penkviksite, is obtained from $\text{SiO}_2\text{-TiO}_2\text{-Na}_2\text{O-H}_2\text{O-(TMA)}_2\text{O}$ and characterized by powder X-ray diffraction (XRD), TGA, SEM, ^{29}Si CP MAS NMR, ion exchange and adsorption measurements.

Titanium silicates such as TS-1,^{1,2} TS-2³ Ti- β ,^{4,5} etc., have attracted considerable research attention since they have been found to have remarkable catalytic activity and selectivity in the hydroxylation of organic compounds in the presence of dilute aqueous hydrogen peroxide. Recently, two novel titanium silicates ETS-4^{6,7} and ETS-10⁶⁻⁸ have been discovered, which have interesting structures and exhibited unique ion-exchange and adsorption properties. More recently, we synthesized a novel layered titanium silicate JDF-LI^{9,10} with five-coordinate titanium, which has potential in catalysis, intercalation and ion-exchange.

There are many natural titanium silicates occurring in the Earth's crust, but only a few such as pharmacosiderite^{11,12} and zorite¹³ could be synthesized. Penkviksite was originally described by Bussen *et al.*,¹⁴ as a new titanosite mineral, with chemical formula $\text{Na}_4\text{Ti}_2\text{Si}_8\text{O}_{22}\cdot 5\text{H}_2\text{O}$ and space group indexed as orthorhombic or monoclinic. After the second polytype was found in nature, the orthorhombic penkviksite was denoted penkviksite-2O and the monoclinic penkviksite as penkviksite-1M.¹⁵ Both penkviksite-2O and penkviksite-1M have minor substitutions of Ca, Zr, Fe and Al for Na, Ti and Si, respectively. The structure consists of TiO_6 octahedra and SiO_4 tetrahedra connected to each other to form a three-dimensional framework.

Here we report, for the first time, the synthesis of a penkviksite-type titanium silicate. The samples were synthesized hydrothermally using tetrabutyltitanium(IV) (98%), tetramethylammonium hydroxide (TMAOH, 25%), fumed silica (99.9%), sodium hydroxide (96%) and distilled water as reactants. The chemical composition of the initial gel was $3.7\text{SiO}_2:5.9\text{TiO}_2:1.0\text{Na}_2\text{O}:100\text{H}_2\text{O}:0.6(\text{TMA})_2\text{O}$. In a typical preparation, the following procedure was followed: sodium hydroxide (0.27 g) was first dissolved in distilled water (12 ml) and then $\text{Ti}(\text{O}i\text{Bu})_4$ (5.1 g) was added slowly to the solution under vigorous stirring, to which aqueous TMAOH (2.5 ml) was added, followed by fumed silica (0.6 g). The mixture was stirred until it became homogeneous, then transferred into a Teflon-lined stainless-steel autoclave, and heated at 473 K for *ca.* 15 days. The products were recovered by filtration, washed and dried at 353 K. The sample was characterized by X-ray diffraction (Rigaku D/MAX-III A), thermal analysis (Perkin-Elmer, TGA-7), scanning electron microscopy (Hitachi X-650B), and ^{29}Si CP MAS NMR (Bruker MSL-400).

The XRD pattern of the as-synthesized crystalline product is similar to that of the mineral penkviksite, but showing different relative intensities (Fig. 1). SEM showed that the sample consisted of plate-like crystals of *ca.* $20 \times 50 \mu\text{m}$ (Fig. 2).

Thermogravimetry of the product showed a total mass loss of 7.8% from 328 to 588 K. This was considered to be mainly due to the removal of waste located on the external surface and in the pores. The product is stable up to 873 K and converts into a dense phase at *ca.* 973 K, as indicated by XRD analysis.

In the ^{29}Si CP MAS NMR study of the as-synthesized penkviksite, three signals with chemical shifts of $\delta -85.2$, -96.0 and -101.6 referenced to tetramethylsilane were

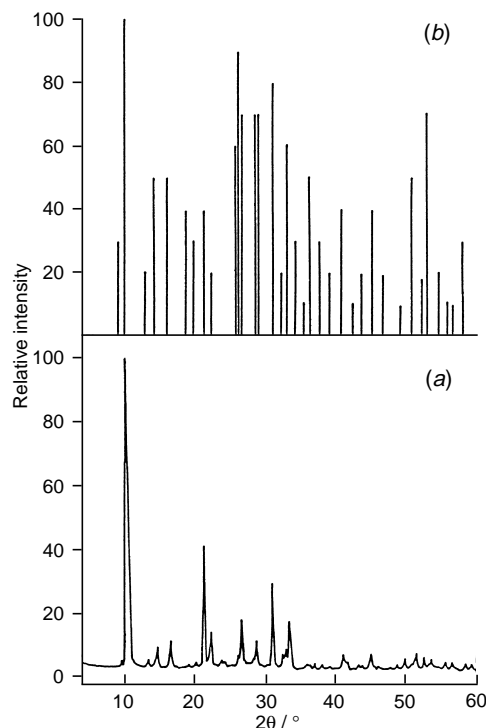


Fig. 1. X-Ray diffraction patterns of (a) as-synthesized penkviksite and (b) the mineral penkviksite



Fig. 2. Scanning electron micrograph of as-synthesized penkviksite

observed. According to refs. 8 and 13, the resonance at $\delta -85.2$ can be attributed to Si(2Si, 2Ti) and that at $\delta -96.0$ to Si(3Si, 1Ti). These assignments are consistent with the framework connectivity of penkvilksite. The additional resonance at $\delta -101.6$ may be due to small amount of impurities in the sample.

The ion-exchange behaviour of penkvilksite was measured in 1 M KNO_3 at 80 °C stirring for 24 h. It was found that 18% of the potassium ions could be exchanged into the penkvilksite. The ion-exchange capacity of K^+ is 0.72 mequiv g^{-1} which is lower than that of other minerals. This may be due to the short reaction time employed.

Adsorption studies were performed isothermally in a Cahn 2000 balance. Before the test, the calcined sample was dehydrated at 473 K at 10^{-3} Torr for 2 h, and then cooled to room temp. under vacuum. Brunauer–Emmett–Teller (BET) adsorption experiments showed type 1 adsorption behaviour and indicated that the adsorption capacity of water was 6.0 mass% at $p/p_0 = 0.2$.

In the synthesis of titanosilicate penkvilksite, we found that alkali-metal ions have an important effect on its formation. In fact, several titanosilicates were produced in $\text{SiO}_2\text{-TiO}_2\text{-M}_2\text{O-H}_2\text{O-(TMA)}_2\text{O}$ ($\text{M} = \text{Na}^+$ or K^+ or $\text{Na}^+ + \text{K}^+$) systems, dependent on the content of alkali-metal ions in the gel. In the presence of K^+ , ETS-10 was readily obtained, while with Na^+ ions alone in the gel, penkvilksite and ETS-4 were synthesized. The former was favoured at low Na^+ concentration and the latter at high Na^+ concentration. In addition, the titanium content was also an important factor for the formation of penkvilksite. Appropriate titanium content in the gel was found to be essential in the crystallization of the pure products. Higher or lower titanium content resulted in the formation of amorphous phases or quartz impurities.

In conclusion, a titanosilicate penkvilksite analogue has been synthesized for the first time under hydrothermal conditions. Its successful synthesis provides possibilities in the synthesis of other new types of titanium silicate materials by varying various

synthesis factors such as alkali-metal ions used, titanium content and templates, etc.

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