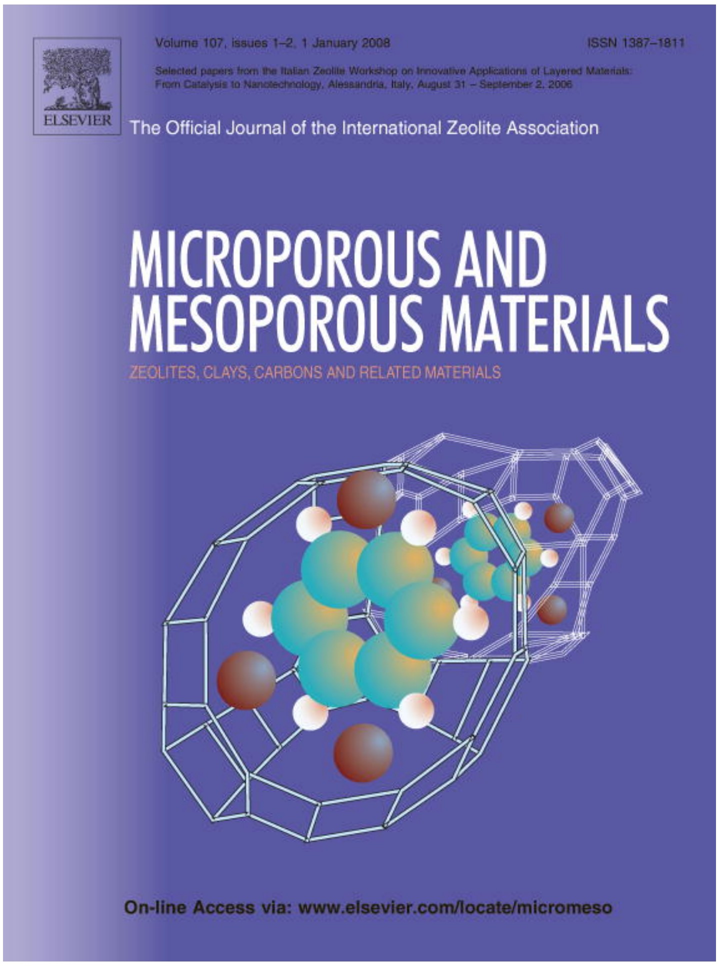

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Layered titanosilicates – A review and some results on the hydrothermal synthesis of bafertisite

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Abstract

Heterophyllosilicates are titanosilicate minerals based on layers which, via a periodic substitution of rows of Si-tetrahedra by rows of Ti-polyhedra, can be formally derived from the tetrahedral–octahedral–tetrahedral (*TOT*) layer of phyllosilicates. According to the periodicity of the substitution, three types of *HOH* layers (*H* to indicate the hetero substitution) are known: bafertisite-, astrophyllite- and nafertisite-type. Based on parallelism between the crystal structures of heterophyllosilicates and phyllosilicates, the paper aims to draw the attention of materials scientists on a possible use of bafertisite-type compounds to produce layered materials of technological interest. Some preliminary results on the hydrothermal synthesis of bafertisite are presented. By EDS electron-microprobe chemical analysis, optical and electron microscopy, and X-ray powder diffraction, a minor presence of bafertisite has been established in a mixture of synthesis products that include gillespite and fresnoite.

Keywords: Heterophyllosilicates; Layered titanosilicates; Hydrothermal synthesis; Bafertisite; Polysomatic series

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1. Introduction

Properties of minerals observed in nature (e.g., porosity in zeolites and other zeolite-like phases [1]) are often directly exploited by modern technologies or may suggest paths to synthesise new materials (e.g., materials based on modular aspects of the crystal structures [2]). In some cases, new synthetic materials are obtained by combining modules of minerals with synthetic compounds to obtain hybrid materials. Layer silicates (phyllosilicates) are a well known source of modules, as well as other layered inorganic compounds [3]. In particular, low-charge tetrahedral–octahedral–tetrahedral (*TOT*) layers of clay minerals, e.g., smectites, are used to prepare organoclay complexes, nanocomposites and pillared materials [4–6].

The main aim of this paper is reviewing a class of layered titanium silicates known as heterophyllosilicates [7] to attract the attention of materials scientists on the possibility of using their *TOT*-like layers for technological applications. The presence of five- and six-coordinated titanium in the layers of the heterophyllosilicates looks particularly appealing, owing to the well known catalytic properties of this chemical element. In the second part of the paper, some preliminary results on the hydrothermal synthesis of bafertisite are presented.

1.1. Heterophyllosilicates, a new class of layered titanosilicates

The determination of the crystal structure of the rare layered titanosilicate nafertisite [8] according to the principles of the modular crystallography [2], suggested [7,9,10] the correlation, via a polysomatic series [2], of a group of titanium silicates that contain *TOT*-like layers and the introduction of the term *heterophyllosilicate*. In the members of the heterophyllosilicate polysomatic series, a row of Ti-polyhedra (or replacing cations, e.g., Nb; hereafter,

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Ti only is mentioned for short) periodically substitutes a row of disilicate tetrahedra within the *T* tetrahedral sheet of a mica *TOT* layer; the octahedral *O* sheet is instead maintained (Fig. 1). *HOH* layers are thus obtained, where *H* stands for *hetero* to indicate the presence of rows of five- or six-coordinated Ti in the modified *T* sheet. A slice of the mica-modified structure with composition $B = A_2Y_4[\mathrm{Ti}_2(\mathrm{O},\mathrm{OH})_4\mathrm{Si}_4\mathrm{O}_{14}](\mathrm{O},\mathrm{OH})_2$ is conventionally named bafertisite-type *B* module. The *B* module may or may not be periodically intercalated (Fig. 1) by unmodified mica modules $M = AY_3[\mathrm{Si}_4\mathrm{O}_{10}](\mathrm{O},\mathrm{OH})_2$; each *M* module is one silicate chain wide. In the formulae of the *B* and *M* modules, *A* and *Y* represent interlayer and octahedral cations, respectively. The resulting polysomatic series is formally represented by B_nM_m. Apart the case $n = 0$, which corresponds to mica, three structure types based on different *HOH* layers are known [10,11] and described in the following.

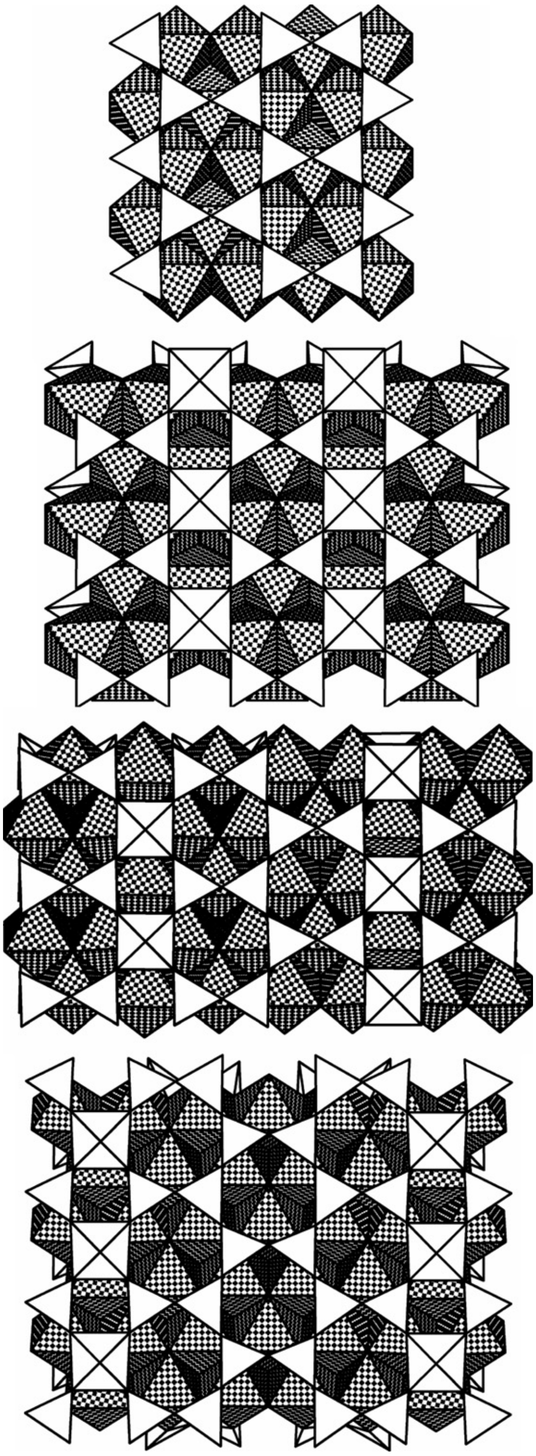

Fig. 1. From top to bottom: *TOT* layer of phyllosicates; bafertisite-type $(HOH)_\mathrm{B}$ layer; astrophyllite-type $(HOH)_\mathrm{A}$ layer; nafertisite-type $(HOH)_\mathrm{N}$ layer. The octahedral *O* sheet of the layers is represented by dotted octahedra; silicate tetrahedra and the octahedra of the *T* and *H* sheets are represented by blank polyhedra.

1.1.1. $(HOH)_B$ bafertisite-type layer

Bafertisite [12,13] is conventionally taken to represent the members B_1M_0 of the series. The corresponding $(HOH)_\mathrm{B}$ layer (Figs. 1, 2) is the most versatile among the known *HOH* layers, being able to sandwich a variety of more or less complex interlayer contents (Table 1). The variety of crystal structures containing the $(HOH)_\mathrm{B}$ layer is by far larger than that known for the structures based on the *TOT* phyllosilicate layer, but the corresponding minerals are rare. The minerals based on the $(HOH)_\mathrm{B}$ layer belong to a series that is known as bafertisite mero-plesiotype series [14] and branches from the general B_nM_m series. The term merotype means that a (nearly) constant module ($(HOH)_\mathrm{B}$ in this case) alternates with a module which is specific of each member [2]; some configurational variability of the $(HOH)_\mathrm{B}$ layer (e.g., five or six coordination of Ti) is indicated by the term plesiotype [2].

The bafertisite series is represented by the general formula $A_2\{Y_4[\mathrm{Ti}_2(\mathrm{O}')_{2+\mathrm{p}}\mathrm{Si}_4\mathrm{O}_{14}](\mathrm{O}'')_2\}W$, where: $[\mathrm{Ti}_2(\mathrm{O}')_{2+\mathrm{p}}\mathrm{Si}_4\mathrm{O}_{14}]^{n-}$ and $\{Y_4[\mathrm{Ti}_2(\mathrm{O}')_{2+\mathrm{p}}\mathrm{Si}_4\mathrm{O}_{14}](\mathrm{O}'')_2\}^{m-}$ correspond to the *H* sheet and the *HOH* layer, respectively.

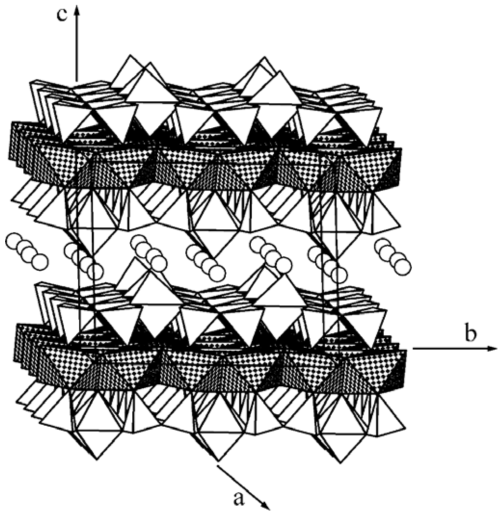

Fig. 2. Crystal structure of bafertisite. *O* and *H* sheets as in Fig. 1. The circles in the interlayer represent Ba atoms.

Table 1
Members of the merotype bafertisite series in increasing order of the *t* cell parameter (either *c* or *a*) across the layers

Name	Chemical formula	t[b]	References[c]
Murmanite	$(Na,\square)_2\{(Na,Ti)_4[Ti_2(O, H_2O)_4Si_4O_{14}](OH,F)_2\} \cdot 2H_2O$	11.70	[25]
Bafertisite	$Ba_2\{(Fe,Mn)_4[Ti_2O_2(O, OH)_2Si_4O_{14}](O,OH)_2\}$	11.73	[12,13]
Hejtmanite	$Ba_2\{(Mn,Fe)_4[Ti_2(O, OH)_4Si_4O_{14}](OH,F)_2\}$	11.77	[26]
Epistolite	$(Na, \square)_2\{(Na,Ti)_4[Nb_2(O, H_2O)_4Si_4O_{14}](OH,F)_2\} \cdot 2H_2O$	12.14	[25]
Vuonnemite	$Na_8\{(Na,Ti)_4[Nb_2O_2Si_4O_{14}](O, OH,F)_2\}(PO_4)_2$	14.45	[27]
Lomonosovite	$Na_8\{(Na,Ti)_4[Ti_2O_2Si_4O_{14}](O, OH)_2\}(PO_4)_2$	14.50	[28]
Yoshimuraite	$Ba_4\{Mn_4[Ti_2O_2Si_4O_{14}](OH)_2\}(PO_4)_2$	14.75	[29]
Innelite	$(Ba,K)_2Ba_2\{(Na,Ca, Ti)_4[Ti_2O_2Si_4O_{14}]O_2\}(SO_4)_2$	14.76	[30]
Phosphoinnelite	$(Ba,Sr)_4\{(Na, Ti)_4[Ti_2O_2Si_4O_{14}](O,F\}(P, S)O_4)_2$	14.76	[31]
Bussenite	$Ba_4Na_2\{(Na,Fe, Mn)_2[Ti_2O_2Si_4O_{14}](OH)_2\}(CO_3)_2F_2 \cdot 2H_2O$	16.25	[32]
Lamprophyllite	$(Sr,Ba)_2\{(Na, Ti)_4[Ti_2O_2Si_4O_{14}]\ (OH,F)_2\}$	19.22	[33]
Nabalamprophyllite	$Ba(Na,Ba)\{(Na,Ti,)_4[Ti_2O_2Si_4O_{14}](OH, F)_2\}$	19.74	[34]
Barytolamprophyllite	$(Ba,Na)_2\{(Na, Ti)_4[Ti_2O_2Si_4O_{14}](OH,F)_2\}$	19.83	[35]
Orthoericssonite	$Ba_2\{Mn_4[Fe_2O_2Si_4O_{14}](OH)_2\}$	20.23	[36]
Quadruphite	$Na_{13}Ca\{(Ti,Na, Mg)_4[Ti_2O_2Si_4O_{14}]O_2\}(PO_4)_4F_2$	20.36	[37]
Ericssonite[a]	$Ba_2\{Mn_4[Fe_2O_2Si_4O_{14}](OH)_2\}$	20.42	[38]
Surkhobite	$(Ca,Na,Ba,K)_2\{(Fe, Mn)_4[Ti_2O_2Si_4O_{14}](F,O,OH)_3\}$	20.79	[39]
Jinshajiangite[a],	$(Na,Ca)(Ba,K)\{(Fe,Mn)_4[(Ti, Nb)_2O_3Si_4O_{14}](F,O)_2\}$	20.82	[40]
Perraultite	$(Na,Ca)(Ba,K)\{(Mn,Fe)_4[(Ti, Nb)_2O_3Si_4O_{14}](OH,F)_2\}$	20.84	[41]
Delindeite	$Ba_2\{(Na,Ti, \square)_4[Ti_2(O, OH)_4Si_4O_{14}](H_2O,OH)_2\}$	21.51	[14]
Polyphite	$Na_{14}(Ca,Mn,Mg)_5\{(Ti,Mn, Mg)_4[Ti_2O_2Si_4O_{14}]F_2\}(PO_4)_6F_4$	26.45	[42]
Shkatulkalite[a]	$\{(Na,Mn,Ca, \square)_4[(Nb, Ti)_2(H_2O)_2Si_4O_{14}](OH,H_2O, F)_2\} \cdot 2(H_2O, \square)$	31.1	[43]
Sobolevite	$Na_{12}CaMg\{(Ti,Na,Mg)_4[Ti_2O_2Si_4O_{14}]O_2\}(PO_4)_4F_2$	40.62	[42]
Bornemanite	$BaNa_3\{(Na,Ti,Mn)_4[(Ti, Nb)_2O_2Si_4O_{14}](F,OH)_2\}PO_4$	47.95	[44]
Bykovaite[a]	$BaNa\{(Na,Ti)_4[(Ti,Nb)_2(OH, O)_3Si_4O_{14}](OH,F)_2\} \cdot 3H_2O$	50.94	[45]

The composition of the heteropolyhedral *H* sheet and *HOH* layer is shown between square brackets and braces, respectively; the composition of the interlayer is outside the braces. The table is derived, with modifications, from [25].

[a] Structure unknown; the inclusion in this table is based mainly on chemical and crystal data.

[b] The unit cells given by authors have been converted to reduced unit cells, if the case.

[c] Reference to the most recent paper describing the structure, when known, otherwise to the paper describing the mineral species.

Besides the already defined *A* and *Y* symbols, *W* represents further interlayer content; O′ (bonded to Ti) and O″ (belonging to the octahedral sheet only) can be an oxygen atom, OH, F or H_2O; the value of *p* (0, 1, 2) depends on the configuration around Ti, which can be either five- or six-coordinated.

1.1.2. $(HOH)_A$ astrophyllite-type layer

Relative to the $(HOH)_B$ layer, in a $(HOH)_A$ astrophyllite-type layer an *M* module is present between two *B* modules. The titanosilicates based on a $(HOH)_A$ layer represent the members B_1M_1 of the heterophyllosilicate B_nM_m polysomatic series and differ each other only by polytypism (i.e., stacking of the layers) and chemical nature of the *A* and *Y* cations [15,16].

1.1.3. $(HOH)_N$ nafertisite-type layer

Relative to the $(HOH)_B$ layer, in a $(HOH)_N$ nafertisite-type layer two *M* modules are inserted between two *B* modules. Nafertisite [7] and caryochroite [17] are the only two known titanosilicates which are based on the $(HOH)_N$ layer; they correspond to the members B_1M_2 of the heterophyllosilicate B_nM_m polysomatic series. Nafertisite and caryochroite differ each other mainly by the chemical composition of the *O* sheet and the water content in the interlayer.

2. Experimental

The minerals of the heterophyllosilicate family are rare, complex in composition, and often intergrown with different phases. Consequently, to investigate the possibility of preparing materials based on *HOH* layers is necessary a preliminary synthesis of some heterophyllosilicates. For our attempts of synthesis, compounds based on the $(HOH)_B$ bafertisite-type layer have been chosen for the reasons given below. The syntheses have been operated under hydrothermal conditions, to approach one (but not the only one; see below) of the genetic conditions observed in nature [18].

The variety of minerals based on the $(HOH)_B$ bafertisite-type layer (Table 1), in comparison with minerals containing the other two types of *HOH* layers, suggests a higher stability for $(HOH)_B$ and consequently, a higher possibility of a successful synthesis. Actually, the only known synthetic heterophyllosilicate is a bafertisite-type silico-vanadate of Ti, $Na_8\{(Na, Ti)_4[Ti_2O_2Si_4O_{14}]O_2\}(VO_4)_2$, which has been obtained from melt [19]. Besides, in nature there are consistent evidences of solid-state transformations from one to another member listed in Table 1 via leaching/substitution of the interlayer composition [18,20,21], thus proving a microporous activity of this type of structure. In particular, the following transformations are reported [18]:

lomonosovite + H_2O → murmanite + Na_3PO_4 and vuonnemite + H_2O → epistolite + Na_3PO_4.

About 100 mg of finely (0.177 mesh) powdered oxides, according to an ideal $BaFe_2TiSi_2O_9$ stoichiometry of bafertisite (cf. Table 1), plus water (6% weight) were sealed within a platinum capsule (0.11 cm^3 in volume). The following chemicals were used: silica gel converted to cristobalite by heating at 1400 °C; titania gel prepared from $TiCl_4$ according to [22], BaO and metallic Fe. Several runs of hydrothermal synthesis were performed in pressure vessels (Tuttle bombs) under a range of conditions: temperature 250–450 °C; pressure 0.08–1.1 Kbar; neutral and, by addition of NaF + NaOH, alkaline conditions; time 160–340 h.

3. Results

The products of synthesis have been characterized by X-ray powder diffraction, optical microscopy, scanning (SEM) and transmission (TEM) electron microscopy with annexed EDS electron microprobes for chemical analysis. Thin lamellar crystals of bafertisite (Fig. 3), mixed with gillespite, $BaFeSi_4O_{10}$, and fresnoite, $Ba_2TiSi_2O_8$, have been observed. The highest presence of bafertisite (~20%) has been obtained in a run performed for 160 h at 380 °C, 1 Kbar, pH 8.5. The content of bafertisite, identified by EDS electron-microprobe analysis, has been evaluated from SEM and optical images. The X-ray powder diffraction patterns of the synthesis products show the presence of peaks in positions expected for bafertisite according to simulated and experimental patterns [13]. For simulation, the structural data obtained for bafertisite in space group *Cm* [12] have been used; in fact, it has been proved [13] that the space group $P2_1/m$ assigned by [23] refers to a substructure. Our powder pattern does not allow a quantitative analysis of the bafertisite content for the following reasons: (i) mixture of at least three phases (bafertisite, gillespite and fresnoite); (ii) as discussed by [13] the peak intensities of the simulated and experimental patterns are very sensitive to the exact chemical composition and preferential orientation.

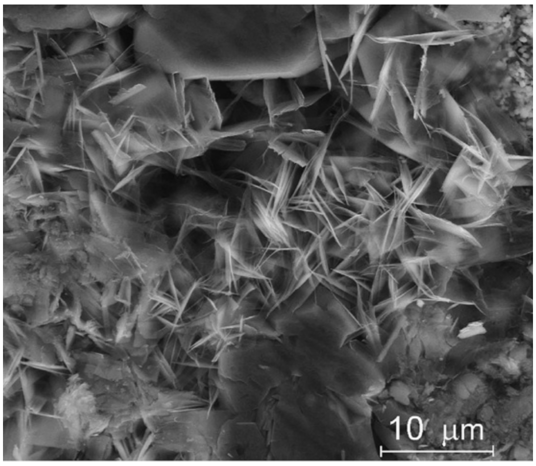

Fig. 3. SEM image of synthetic bafertisite.

4. Conclusions

The preliminary results here reported show that bafertisite can be synthesized under hydrothermal conditions, but more work is necessary to establish experimental conditions that allow a higher yield. In fact, under the conditions so far investigated, the starting chemicals completely react, but a mixture of phases crystallizes. Taking into account the variety of isomorphous replacements, which are evident even in the simplified formulae given in Table 1, one can reasonably suspect that ideal end members are not the favoured phases: likely, addition of minor elements is necessary to improve the yield of the wanted phase.

The structural parallelism between layer silicates (e.g., smectites) and heterophyllosilicates leads to speculate on a possible use of *HOH* layers (Fig. 1) to produce technological materials analogous to well known layered materials based on *TOT* layers (e.g., mesoporous pillared clays [24], organoclays and clay nanocomposites). The presence of Ti in the layers adds interest. However, since the heterophyllosilicates have been overlooked so far by materials researchers, no records of their use as precursors of synthetic layered materials are known.

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