Tb/Na tobermorite: Thermal behaviour and high temperature products

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ABSTRACT

By heating a sample of Tb/Na tobermorite we obtained a phase which was identified through its X-ray diffraction (XRD) pattern, as terbium silicate apatite. Subsequently this compound has been directly prepared by solid state reaction and we carried out a structural refinement from XRD data in space group $P6_3/m$ obtaining cell parameters $a = 9.39199(4)$ Å and $c = 6.84041(5)$ Å. Terbium silicate apatite heated in melted NaF led to Tb_4O_7 crystals.

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1. Introduction

Tobermorite—more precisely tobermorite 11 Å—is a microporous calcium silicate which has been firstly found as a natural phase in three localities of Scotland, two near Tobermory, Mull island, and one at Dunvegan, Skye island [1] and presents chemical composition $Ca_{5-x}Si_6O_{17-2x}(OH)_{2x} \cdot 5H_2O$, where x varies between 0 and 1 [2]. The interest in the structure and crystal chemistry of tobermorite compounds stemmed from their close relationships with the C–S–H phases formed during the hydration processes of Portland cement [3], as well as from their properties as cation exchangers and potential applications in nuclear and hazardous waste disposal: the cation exchange and selectivity properties of tobermorite 11 Å have been firstly noticed by Komarneni et al. [4], who observed that an exchange capability is mainly exhibited by (Al+alkali)-substituted tobermorite 11 Å, which, moreover, shows high selectivity for cesium cations.

Tobermorite formation has been observed during the processing of autoclaved aerated concrete coming from blast furnace slag [5]. The use of synthetic tobermorite fibres has been recently proposed as whiskers for the production of heat insulating and fire resistant building materials [6]. Other possible applications of tobermorite recently proposed are connected with their mechanical properties, exploited in the packing field [7], or with their adsorption ability exploited in the phosphorous removing from waste waters [8].

Interesting photoluminescence properties are presented by the sodium lanthanide silicates with the structure type of tobermorite 11 Å firstly prepared by Ferreira et al. [9] and whose thermal behaviour is the main object of the present paper.

The structure of tobermorite 11 Å is composed by wollastonite-like chains connected to build double chains linked to both sides of sevenfold coordinated Ca^{2+} polyhedral layers [10]. The distance between adjacent calcium layers is 11.3 Å, and this explains the name *tobermorite* 11 Å used to distinguish it from other phases of the same family characterized by different basal spacing. The double wollastonite chains and the calcium polyhedral layers build up a framework presenting 'zeolitic channels' containing H_2O molecules and a variable amount of Ca^{2+}, ranging from 0 to 1 atoms per formula unit. Most of tobermorite 11 Å samples heated at 300 °C for few hours transform on dehydration to *tobermorite* 9 Å [2], $Ca_5Si_6O_{16}(OH)_2$, another phase of the same family but with a basal spacing of 9.3 Å. Some tobermorite 11 Å samples do not shrink on dehydration at 300 °C, and their thermal behaviour was called 'anomalous' in contrast to the 'normal' one described above. In 'anomalous' samples a lower calcium content was observed, and it was supposed that the 'zeolitic' Ca^{2+} amount would determine the thermal behaviour of tobermorite 11 Å [2]. In fact, Ca^{2+} ions contained in channels lose on dehydration some H_2O molecules which they were linked to, and so, if 'zeolitic' Ca^{2+} amounts are high enough, decondensation of the double chains and consequent approach of adjacent layers are favoured so that the coordination sphere of these cations may be completed by oxygen atoms of the framework. By further heating tobermorite 9 Å, from 450 to 650 °C it dehydrates more, and there is a gradual increase in basal spacing up to 9.7 Å. At 730–775 °C an

intermediate wollastonite-like phase forms, and it transforms to wollastonite, $CaSiO_3$, at 850–900 °C.

Ferreira et al. [9] prepared compounds with ideal formula $KNa_2Ln_2Si_6O_{16}(OH)\cdot 3H_2O$ (Ln = Eu, Ce, Sm, Tb, Eu/Tb and Tb/Gd) structurally analogue to tobermorite 11 Å, but containing trivalent lanthanide cations and Na^+, substituting for calcium in polyhedral layers, and K^+ (and a small amount of Na^+, too) as 'zeolitic' cations. These phases, called AV-20 materials, showed 'anomalous' thermal behaviour: adjacent layers did not approach on dehydration at 300 °C, and so the basal spacing was kept at about 11 Å.

The present paper reports the study of thermal behaviour of a terbium-containing phase, which, as those described above, is structurally analogue to tobermorite 11 Å. The paper describes the structure of its high temperature heating product, which resulted to be a Na, Tb silicate apatite, and presents the synthesis of this compound from the components.

2. Experimental

2.1. Tb/Na tobermorite

Tb/Na tobermorite was prepared by hydrothermal reaction (heating at 230 °C for 3d in a teflon-lined autoclave) and it was determined, through X-ray fluorescence analyses and a structural study carried out from powder X-ray diffraction (XRD) data, that its crystal chemical formula was $|Na_{0.8}(H_2O)_x|[Na_2Tb_2Si_6O_{15.8}(OH)_{1.2}(H_2O)_2]$ ($x = 1-2$). Powder XRD pattern in Bragg-Brentano geometry was collected on a Philips PW1050/25 diffractometer with Cu$K\alpha$ radiation and a secondary beam graphite monochromator and operating at 40 kV and 20 mA. The powder pattern of Tb/Na tobermorite was collected on a sample of measured thickness of 1 mm, in a crystalline quartz sample holder, by the step counting method in the range 4°–60° 2θ with steps of 0.02° and time 17 s/step (Fig. 1). Some samples were then heated in alumina crucible using a simultaneous TG-DSC running on Netzsch 449C thermoanalyser (inert atmosphere with N_2 flow of 30 mL/min, heating rate 10 °C/min, analysis range 20–1000 °C), connected to a mass spectrometer. The powder pattern of the sample heated at 320 °C was collected on a thin layer, placed on crystalline quartz slab, by the same method described above. From this diffraction pattern it resulted there was no meaningful change of basal spacing, which was kept at about 11 Å. Therefore Tb/Na tobermorite, like AV-20 materials, shows 'anomalous' thermal behaviour. The powder patterns of samples heated at 950 and 1200 °C (Fig. 1), measured in the same way, were similar to the ones of phases with apatite-type structure prepared by
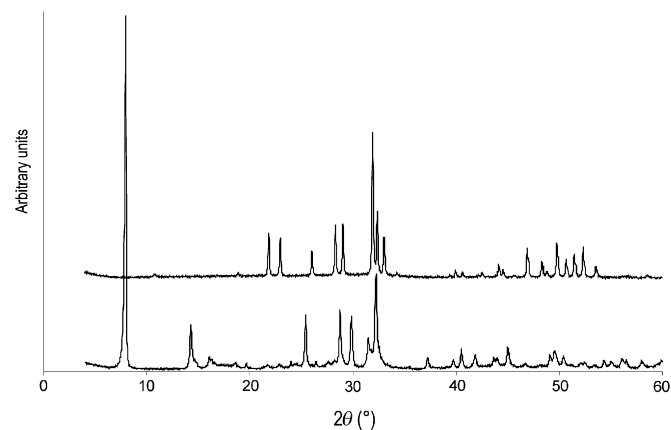
Felsche in 1972 [11]. The chemical formula of the compound could be $NaTb_9(SiO_4)_6O_2$ or $Tb_{9.33}\square_{0.67}(SiO_4)_6O_2$, where $\square$ indicates a structural vacancy. In both cases at least another phase have to form because these stoichiometries are different from the one of Tb/Na tobermorite, and that phase is probably a sodium silicate we have to suppose amorphous because it does not appear in the powder pattern.

2.2. Terbium silicate apatite

To carefully verify the nature of the phase produced by heating Tb/Na tobermorite at high temperature, we synthesized terbium silicate apatite having formula $NaTb_9(SiO_4)_6O_2$ using the method described by Felsche: 885 mg Tb_2O_3 (2.4 mmol, Sigma Aldrich, purity 99.99%), 212 mg SiO_2 (3.2 mmol, Carlo Erba) and 30 mg Na_2CO_3 (0.3 mmol, Carlo Erba, purity 99.7%) were hand-milled in an agate mortar; the resulting powder was pressed at about 200 bar, and the tablets so produced were put in a platinum crucible and heated in a Lenton UAF 16/5 muffle furnace at 1100 °C for 21–22 h. Tablets were hand-milled in the agate mortar and the powder was pressed again; tablets were heated a second time for about 16 h. Tablets have then been milled in acetone and the powder, after drying, was heated at about 200 °C for 2 h. We have then recorded a powder XRD pattern in Bragg–Brentano geometry of a sample with measured thickness of 1 mm in a plexiglas sample holder, by the step counting method in the range 10°–120° 2θ with steps of 0.02° and time 30 s/step in the range 10°–41.5°, 40 s/step in the range 41.5°–81° and 60 s/step in the range 81°–120°. A comparison of this diffraction pattern with those of the samples obtained by heating Tb/Na tobermorite at 950 °C and at 1200 °C, indicated that in all cases we are dealing with the same phase. From these powder data we carried out a structural refinement with the Topas program in the space group $P6_3/m$; we fitted the profile by Le Bail's method and we obtained cell parameters $a = 9.39199(4)$ Å and $c = 6.84041(5)$ Å [12]. To refine the atomic parameters we used as a model the structure described by Kahlenberg and Krüger for the phase of formula $La_{9.71}(Si_{0.81}Al_{0.19}O_4)_6O_2$ [13]. In the refinement no sodium atom was introduced due to its relatively low scattering power and its mixing with Tb in a definite site. Moreover constraints were imposed on bond length Si–O, fixed to 1.60 Å, on the distance between terbium and oxygen atoms, set up at 2.28 Å, and on isotropic displacement parameters, which had to be equal for all atoms of the same element.

To obtain a single crystal of terbium silicate apatite of a suitable size for X-ray data collection, we tried to recrystallize it from melted NaF. We carried out X-ray data collection on one of the crystals obtained with this trial and we found out it was of the terbium oxide with formula Tb_4O_7, having a fluorite-type defective structure [14].

3. Structure description and discussion

Experimental and calculated powder patterns are compared in Fig. 2. From the structural refinement the atomic coordinates, the occupancies and the displacement parameters reported in Table 1 were obtained.

Sodium is located in the mixed-occupancy site indicated as Tb2. No sodium atom was introduced in the refinement; sodium content was established on the basis of the occupancy of this site. Sodium has an X-ray scattering power of about 11/65 of terbium one. Supposing that in the four positions of this site there are either Tb or Na atoms, in a refinement not considering sodium presence, the occupancy would result: $[x\cdot 65+(1-x)\cdot 11]/65 = 0.787$, where x is the ratio between number of Tb atoms

Fig. 1. XRD patterns of Tb/Na tobermorite (below) and of the product obtained after heating at 1200 °C (over).
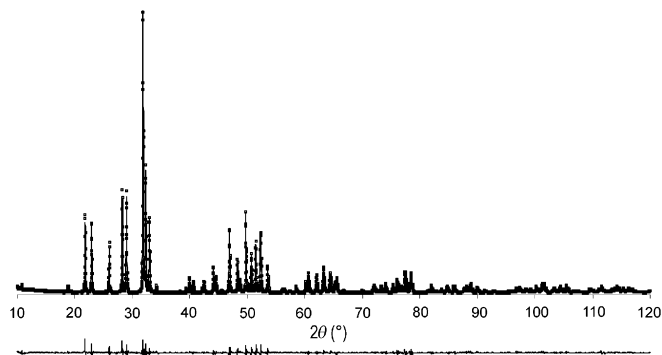
Fig. 2. XRD patterns of terbium silicate apatite: little squares, experimental; continuous line over, calculated; continuous line below, difference.

Table 1

Atomic coordinates, occupancies and isotropic displacement parameters for terbium silicate apatite.

	Wyckoff symbol	x	y	z	Occupancy	B_{eq} (Å²)
Si	6h	0.3985(7)	0.0250(9)	0.75	1	0.8(1)
Tb1	6h	0.2323(2)	0.2395(2)	0.75	1	0.51(2)
Tb2	4f	1/3	2/3	0.5029(6)	0.787(2)	0.51(2)
O1	6h	0.325(2)	−0.172(2)	0.75	1	1.1(1)
O2	12i	0.3357(9)	0.0862(9)	0.566(1)	1	1.1(1)
O3	2a	0	0	0.75	1	1.1(1)
O4	6h	0.600(2)	0.128(2)	0.75	1	1.1(1)

Table 2

Selected interatomic distances (Å) and angles (°) for terbium silicate apatite[a].

Si–O2	1.613(9) × 2	Si–O1	1.621(13)
Si–O4	1.637(13)	Tb1–O3	2.2160(11)
Tb1–O2^{i}	2.317(7) × 2	Tb1–O4^{ii}	2.408(18)
Tb1–O2	2.449(9) × 2	Tb1–O1^{iii}	2.744(14)
Tb2–O1^{iii}	2.297(11) × 3	Tb2–O4^{i}	2.430(10) × 3
Tb2–O2^{i}	2.839(6) × 3		
O2–Si–O2^{iv}	102.6(7)	O1–Si–O2	112.5(4) × 2
O1–Si–O4	112.4(8)	O2–Si–O4	108.1(4) × 2
O3–Tb1–O2^{i}	103.7(2) × 2	O2^{i}–Tb1–O2^{v}	137.8(3)
O2^{v}–Tb1–O4^{vi}	85.5(3) × 2	O3–Tb1–O4^{vi}	151.4(3)
O2–Tb1–O4^{vi}	72.3(3) × 2	O2–Tb1–O2^{v}	137.6(3) × 2
O2–Tb1–O2^{i}	77.22(13) × 2	O2–Tb1–O3	83.22(17)
O2–Tb1–O2^{iv}	61.9(4)	O2–Tb1–O1^{iii}	146.6(2) × 2
O1^{iii}–Tb1–O4^{vi}	97.4(4)	O2^{i}–Tb1–O1^{iii}	70.20(16) × 2
O3–Tb1–O1^{iii}	111.3(3)	O1^{iii}–Tb2–O1^{vi}	71.8(5) × 3
O1^{vii}–Tb2–O4^{i}	153.4(3) × 3	O1^{vi}–Tb2–O4^{i}	94.6(4) × 3
O1^{iii}–Tb2–O4^{i}	126.6(4) × 3	O4^{i}–Tb2–O4^{viii}	74.9(4) × 3
O4^{viii}–Tb2–O2^{i}	124.9(3) × 3	O4^{i}–Tb2–O2^{viii}	65.4(4) × 3
O4^{viii}–Tb2–O2^{iii}	59.3(3) × 3	O1^{vii}–Tb2–O2^{i}	139.6(3) × 3
O1^{vi}–Tb2–O2^{i}	88.2(3) × 3	O1^{vi}–Tb2–O2^{viii}	68.7(4) × 3
O2^{i}–Tb2–O2^{viii}	117.30(10) × 3		

[a] ^{i}indicates $x−y$, x, $1−z$; ^{ii} indicates $1−x+y$, $−x$, z; ^{iii} indicates $−y$, $x−y$, z; ^{iv} indicates x, y, $3/2−z$; ^{v} indicates $x−y$, x, $1/2 −z$; ^{vi} indicates $1−x + y$, $1−x$, z; ^{vii} indicates x, $1+y$, z and ^{viii} indicates $1−x$, $1−y$, $1−z$.

and total number of atoms. The solution of the above formula is $x \cong 0.743$, which is in good agreement within experimental errors with the expected values (0.75 Tb and 0.25 Na in this site). On the basis of site multiplicity (6 for Si, 6 for Tb1, 4 for Tb2, 6 for O1, 12 for O2, 2 for O3 and 6 for O4), we can deduce the unit cell content is that indicated by the formula $NaTb_9(SiO_4)_6O_2$. In Table 2 selected interatomic distances and bond angles are reported.

The bond length values obtained by the present study compare well with the results obtained in the single-crystal study of the isostructural compound $NaY_9(SiO_4)_6O_2$ [15].
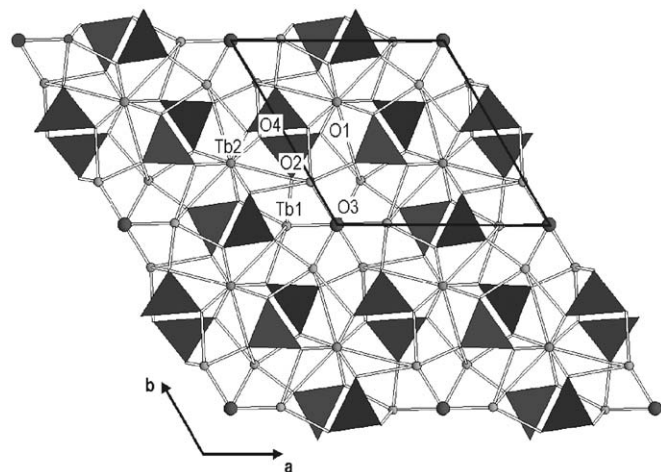

Fig. 3. Projection along c of terbium silicate apatite.

The metal atoms in position 4f are ninefold coordinated by silicate O atoms. The coordination polyhedron is a distorted tricapped trigonal prism.

O3 is the 'free' oxygen atom, that is not bonded to Si atoms. Three Tb1 atoms are bonded to this oxygen, and they form an equilateral triangle around it. The Tb1 atoms are bonded to six silicate O atoms and to O3. The coordination geometry is that of a distorted pentagonal bipyramid, and O3 occupies one of the apical positions.

The structure is reported in Fig. 3.

4. Conclusions

Unlike tobermorite 11 Å s.s. (*sensu stricto*), which heated at 850–900 °C converts to wollastonite, Tb/Na tobermorite, containing Na$^+$ and Tb^{3+} instead of Ca^{2+} transforms to a terbium silicate apatite of formula $NaTb_9(SiO_4)_6O_2$ when heated at high temperature. These two phases produced by high temperature heating are structurally very different from each other. In wollastonite, in fact, the silicate chains called 'Dreiereinfachketten', according to Liebau [16] terminology, which have a repetition period of three tetrahedra and are formed by pairs of tetrahedra linked by a bridging tetrahedron, are still present, although as single chains at difference from the double chains which characterize the crystal structure of tobermorite 11 Å. In wollastonite, Ca^{2+} ions not only form ribbons, with silicate chains grasped on both sides of them, instead than infinite layers, but also the single calcium polyhedra are quite different from those occurring in tobermorite 11 Å. In the silicate apatite produced by heating Tb/Na tobermorite, silicate anions are present as isolated SiO$_4$ tetrahedra, so a complete fragmentation of the chains of the tobermoritic phase must occur. Furthermore, in the wollastonite structure, every oxygen is bonded to silicon atoms, whereas in silicate apatite there is also an oxygen atom which is bonded to no silicon atom. In the apatitic phase, coordination polyhedra of metallic cations are isolated, too, with the exception of Tb1 ones, which form groups of bipyramids correlated by a threefold rotation axis and sharing an apical corner, just corresponding to the oxygen atom which is bonded to no silicon atom.

As already said, Tb/Na tobermorite shows 'anomalous' behaviour on heating at 320 °C. This phase presents sodium cations in the 'zeolitic' channels and, on the basis of tobermorite 11 Å with similar content of 'zeolitic' calcium cations ([2,10]) we would foresee a normal behaviour on dehydration at 300 °C, namely a shrinking of the framework with transformation to tobermorite

9 Å to preserve a proper coordination for the sodium cations. However it appears evident that, notwithstanding the very similar ionic radii, the crystal chemical behaviour of sodium and calcium cations may be quite different. In particular, at difference from what happens with 'normal' tobermorite 11 Å, the dehydration of the Tb/Na tobermorite does not require a shrinking of the framework: the 'zeolitic' sodium cations, deprived of the co-ordinated water molecules, most probably are displaced toward the inside walls of the framework to acquire an acceptable threefold or fourfold coordination. An example of the stability of sodium cation in such a low coordination is an erbium and sodium disilicate, $Na_3ErSi_2O_7$, we have obtained in a work related to the present one [14]: actually in this phase there is a sodium atom in a threefold coordination.

The distinct behaviour of zeolites containing Ca^{2+} and Na^+ cations on dehydration gives a strong support to our explanation of the anomalous behaviour of Tb/Na tobermorite. In fact whereas T–O–T breaking upon dehydration has been observed in zeolite structures containing Ca^{2+} cations (more generally cations with high ionic strength), dehydration of zeolites containing Na^+ as extra framework cations does not cause T–O–T breaking [17,18].

Acknowledgments

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