JOURNAL OF MATERIALS SCIENCE **39** (2004) 4343–4344 LETTERS

A rapid method for low-temperature synthesis of the Na analogue of the microporous titanosilicate GTS-1

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The synthesis of Grace titanium silicate-1 (GTS-1-$K_{2.3}H_{1.7}(Ti_{4.0}Si_{4.0})O_x$; $Cs_{3.7}H_{0.3}(Ti_{4.0}Si_{3.6})O_x$), which is a synthetic analogue of the cubic mineral pharmacosiderite $KFe_4(OH)_4(AsO_4)_3$, was for the first time reported by Chapman and Roe [1]. A later report [2] described the synthesis of a cesium form of GTS-1 and its single-crystal structure refinement. Using powder X-ray diffraction Behrens *et al.* [3] studied the structure of pharmacosiderite analogues of $HM_3Ti_4O_4(SiO_4)_3{\cdot}4H_2O$ ($M = H^+$, K^+, Cs^+) composition. These titanosilicate materials are composed of alternating TiO_6 octahedra and SiO_4 tetrahedra in three orthogonal directions, thus creating a cube-like, three-dimensional tunnel structure whose pore openings are approximately 3.5 Å wide [3, 4]. Water molecules reside within these tunnels and the exchangeable cations sit in the face centers of the cube [2, 4]. The GTS-1 porous structure allows ion exchange as is demonstrated by its selectivity for Sr^{2+} and Cs^+ in the presence of ppm levels of Ca^{2+}, Mg^{2+}, K^+ and Na^+ in slightly acid to neutral solutions [3, 4]. The high affinity of this exchanger for Cs^+ and Sr^{2+} makes it a promising material for the remediation of ground-water or certain types of nuclearwaste [3, 4]. Recently, it was suggested to use this material for preparing thin films and membranes where small crystal size of the run product is required [5].

Capman and Roe [1] have synthesized potassium and cesium forms of GTS-1 at 200 °C for 48 h using organic reactants as a template and source of titanium. Harrison *et al.* [2] succeeded in growing single crystals at high temperatures (750 °C) and pressures (≈30000 psi). Kuznicki and co-workers [6] reported GTS-1 obtained from a sodium batch after one day at 200 °C, using titanium butoxide as a source of titanium. Mintova *et al.* [5] presented a synthesis of pharmacosiderite analogue realized after 5 days at 180 °C using tetramethylammonium hydroxide as a template and an initial sodium-potassium batch. Synthesis of a new rombohedrally distorted pharmacosiderite—type titanosilicate $Na_4[(TiO)_4(SiO)_4]{\cdot}6H_2O$, prepared at 160 °C for 100 h has also been reported [7]. All the above workers report that reaction temperatures between 160 and 750 °C and reaction time of 40–120 h are necessary for the crystallization of titanosilicate analogues of the mineral pharmacosiderite.

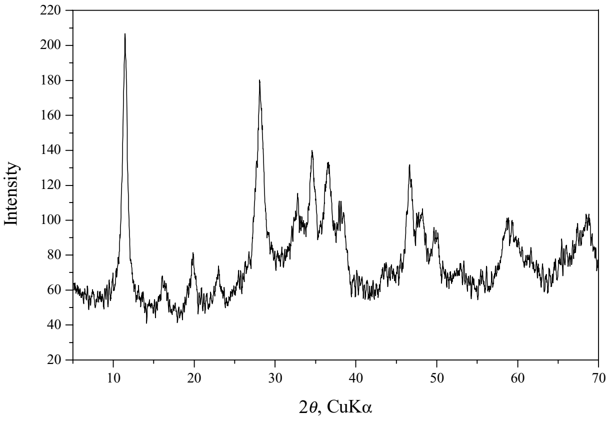

Figure 1 Powder XRD pattern of the as synthesized GTS-1.

The present paper reports a new approach for synthesis of microporous titanosilicates. We describe the synthesis of GTS-1 from a sodium gel at 90 °C after 18 h, without using any organic reactants.

The hydrothermal syntheses of GTS-1 were carried out from gels of the following molar compositions: 17–20 Na_2O : 2.5–3.5 TiO_2 : 10 SiO_2: 675 H_2O. In a typical synthesis, 3.0 g SiO_2 (Sigma) of 12 μm particle size was added to a heated solution of 7.1 g NaOH (Fluka) in 40 ml distilled water. Subsequently, 1.6 ml $TiCl_4$ (Fluka) was added to the above solution. The mixture was homogenized for 120 min by a mechanical mixer at 300 rpm. Then, the gel was transferred into a 250 ml Teflon-lined autoclave. The crystallization was performed under static conditions at 90 °C for 18 h. After fast cooling with flowing water the sample obtained was filtered with distilled water and dried at 50 °C for 24 h.

The powder XRD pattern (Fig. 1) of the synthesized material was collected in a step-scan regime

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TABLE I Powder X-ray diffraction data for the as synthesized GTS-1

$2\theta_{\text{obs}}$	I_{h}	$d_{(\text{obs})}$	hkl	$d_{(\text{calc})}$	$\delta 2\theta$
11.495	100	7.6983	100	7.7566	−0.087
16.116	11	5.4999	110	5.4847	0.045
19.891	18	4.4638	111	4.4783	−0.065
23.015	11	3.8643	200	3.8783	−0.084
28.170	67	3.1678	211	3.1666	0.011
32.718	26	2.7371	220	2.7424	−0.064
34.656	41	2.5884	221	2.5855	0.040
			300	2.5855	0.040
36.620	38	2.4540	310	2.4529	0.018
38.438	27	2.3420	311	2.3387	0.056
43.599	7	2.0760	321	2.0730	0.065
46.827	36	1.9401	400	1.9391	0.025
48.331	27	1.8832	410	1.8813	0.053
			322	1.8813	0.053
49.881	18	1.8283	330	1.8282	0.000
			411	1.8282	0.000
52.735	6	1.7358	420	1.7344	0.046
58.229	25	1.5845	422	1.5833	0.047
60.931	4	1.5205	510	1.5212	−0.029
			431	1.5212	−0.029
66.046	12	1.4146	521	1.4162	0.081
68.452	26	1.3707	440	1.3712	−0.030
69.521	6	1.3996	261	1.3997	−0.006

(step 0.02 ° and time 1 s) on a PW3710 diffractometer with Cu K_α radiation in the range 2θ, 5–70 °. The XRD pattern is similar to that reported by other workers [1–5] and it unambiguously identified the phase as being GTS-1 (PDF 47-0043, 86-665-potassium forms). The primary powder XRD data standardization, interpretation, and presentation of GTS-1 were performed with the PDI package [8], which provides indexation for known unit cell parameters and refinement of the latter. Table I lists the indexed powder XRD data of GTS-1 with figure of merit $F_{18} = 14.15$ (0.047, 27). The refined unit cell parameter in space group P-43m (no. 215) is $a = 7.757(3)$ Å, which is smaller than the one reported before for the K analogues (PDF 47–0043, 86–665) and the Cs form [1, 2], which results from the smaller ionic radius of the sodium ion. The broadness of the measured peaks suggests a particle size of about 11 nm (calculated with the Sherrer formula using PC-APD [9], which suggests new possibilities for using this material.

Acknowledgment

This work was realized with the financial support by a Marie Curie Fellowship of the European Community under contract number HPMT-GH-00138-07 and by the National Science Fund—Bulgarian Ministry of Education and Science under contract number NT 1-02.

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Received 23 October
and accepted 30 December 2003