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A rapid method of synthesizing the layered titanosilicate JDF-L1

Stanislav Ferdov,[a] Vladislav Kostov-Kytin*[b] and Ognyan Petrov[b]

[a] *Marie Curie Fellowship of the European Community, Institute of Mineralogy and Crystallography, University of Vienna, Vienna, Austria*

[b] *Central Laboratory of Mineralogy and Crystallography, Bulgarian Academy of Science, bl.107, Academic G. Bonchev Str., No 2, 1113 Sofia, Bulgaria. E-mail: vkytin@mail.bg; Fax: (+359 2) 979 70 56*

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A rapid procedure for synthesis of highly crystalline and pure samples of JDF-L1 without using organics as reactants or templates is described and indexation of the powder X-ray diffraction pattern of this phase is presented.

The novel layered titanosilicate AM-1 was firstly reported in 1995.[1] The later synthesis and structural determination of a phase named JDF-L1 showed that it is a structural counterpart of AM-1 with the same chemical composition—$Na_4Ti_2Si_8O_{22}\cdot 4H_2O$.[2–6] This is an unusual non-centrosymmetric, tetragonal layered solid. Its structure contains titanosilicate layers built of small cage-type units, each one containing eight tetrahedral SiO_4 units and one square-pyramidal TiO_5 polyhedron. Two of these layers are separated by a layer of water molecules sandwiched between two layers of Na^+ ions.[5] The JDF-L1 layered structure allows pillaring as demonstrated by the successful intercalation of nonylamine.[4] Intercalation with bigger molecules could provide specialized use for this material as catalyst, catalyst support, ion exchanger, *etc.* Furthermore, the five-coordinated titanium(IV) is of less ligand saturation in comparison with the octahedrally-coordinated one known in the structures of other microporous and layered titanosilicates.[6] This makes JDF-L1 a promising material for oxidation catalysis. JDF-L1 was synthesized by Roberts *et al.*[4] using organic reactants as template and source of titanium. In the synthesis of AM-1, Anderson and co-workers[1,2] used $TiCl_3$ as the source of Ti. All the above workers have reported that 4 to 10 days are necessary for the crystallization of the phase. We now report the synthesis of JDF-L1 over a very short reaction time (<16 h) using $TiCl_4$ and in the absence of organic reactants or templates.

The hydrothermal syntheses of JDF-L1 were carried out from gels of the following molar composition: 5–6 $Na_2O:1–1.3$ $TiO_2:10$ $SiO_2:675$ H_2O. The preparation of pure JDF-L1 appeared to be quite sensitive toward the grade of the reactants used and the ratio Na_2O/TiO_2 in the initial batches. Increased values of the latter bring to the formation of crystalline aggregates of ETS-4, which is a microporous titanosilicate phase.[6] Lowering of these values leads to the appearance of quartz in the run product. In a typical synthesis, 1.48 g SiO_2 (Merck) of 200 μm particle size was added to a solution of 1.1

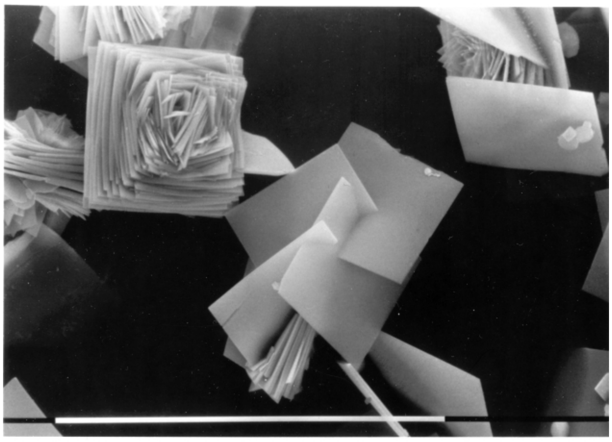

Fig. 1 SEM micrograph of JDF-L1 aggregates. Bar = 100 μm.

Table 1 Powder X-ray diffraction data for the as synthesized JDF-L1

$2\theta_{obs}$	I_h	$d_{(obs)}$	*hkl*	$d_{(calc)}$	$\delta 2\theta$
9.662	100	10.6733	001	10.6983	−0.023
16.958	5	6.0711	101	6.0703	0.002
19.264	100	5.3498	002	5.3491	0.002
21.999	1	4.6916	111	4.6860	0.207
23.881	35	4.3265	102	4.3295	−0.016
27.746	2	3.7334	112	3.7332	0.001
28.130	8	3.6834	200	3.6859	−0.020
29.073	38	3.5663	003	3.5661	0.002
29.782	21	3.4833	201	3.4849	−0.014
31.534	1	3.2943	210	3.2968	−0.025
32.392	16	3.2093	103	3.2102	−0.010
32.995	17	3.1523	211	3.1506	0.018
34.282	2	3.0372	202	3.0351	0.25
35.413	1	2.9432	113	2.9433	0.000
37.176	6	2.8082	212	2.8066	0.022
40.161	7	2.6072	220	2.6063	0.013
40.898	3	2.5622	203	2.5629	−0.013
41.715	8	2.5142	104	2.5142	−0.001
44.184	5	2.3801	114	2.3796	0.010
46.296	1	2.2771	311	2.2777	−0.013
49.451	1	2.1401	005	2.1397	0.011
50.369	3	2.1036	223	2.1042	−0.016
51.673	12	2.0540	105	2.0549	−0.023
54.619	2	1.9511	313	1.9513	−0.005
55.921	1	1.9092	322	1.9098	−0.021
57.839	2	1.8511	205	1.8505	0.021
58.114	3	1.8431	400	1.8430	0.004
59.861	2	1.7941	215	1.7948	−0.027
60.271	3	1.7830	006	1.7830	−0.002
60.609	4	1.7740	323	1.7737	0.010
61.255	2	1.7571	314	1.7573	−0.011
64.094	4	1.6870	116	1.6871	−0.003
65.755	3	1.6490	420	1.6484	0.27
66.690	1	1.6285	421	1.6292	−0.031
67.797	1	1.6050	206	1.6051	−0.005
69.571	3	1.5690	216	1.5684	0.035
71.721	2	1.5280	007	1.5283	−0.015
73.460	1	1.4968	107,423	1.4964	0.017
74.563	3	1.4778	325	1.4782	−0.024

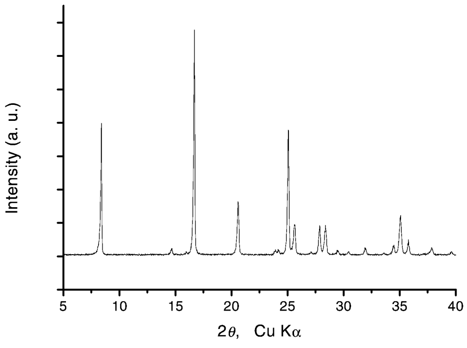

Fig. 2 Powder XRD pattern of the as synthesized JDF-L1.

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g NaOH (Merck) in 20 ml distilled water. Then the solution was brought to the boiling point. Subsequently, 0.33 ml $TiCl_4$ (Merck) hydrolyzed in 10 ml distilled water was added to the above solution. After cooling to room temperature the mixture was homogenized for 40 min by a mechanical mixer at 200 rpm. The gel was then transferred into 10 ml teflon-lined autoclaves. The crystallization was performed under static conditions at 200 °C for 16 h. After fast cooling with flowing H_2O the samples were filtered and washed with distilled water and dried at 100 °C for 2–3 h.

SEM studies (SEM Philips 515) of the run product display 30–40 μm aggregates built of more or less spatially oriented crystal plates (Fig. 1). The XRD powder pattern was collected in a step-scan regime (step 0.02° and time 3 s) on a PW3710 diffractometer with CuK_α radiation in the range 2θ 5–70° and unambiguously identified the phase as being JDF-L1 (Fig. 2). Indexation and cell parameters refinement were performed using strip-chart powder XRD data recorded on DRON 3M (Russia) diffractometer (Fe-filtered CoK_α radiation, λ = 1.7903 Å, room temperature). The measurement was performed at 1° 2θ min^{-1} detector speed (scintillation counter) and 720 mm h^{-1} chart speed in the range 2θ 8–75°. The primary powder XRD data standardization, interpretation, and presentation of JDF-L1 were performed with PDI package,[7] which provides indexation for known unit cell parameters[4] and refinement of the latter by a nonlinear least-squares procedure for minimizing the SUM $[Q\,(\mathrm{exp}) - Q\,(\mathrm{cal})]^2$: $Q = 1/d^2$. Table 1 contains data of the indexed powder pattern of JDF-L1 with figures-of-merit F_{30} = 46.41 (0.013, 49) and M_{20} = 50.84. The refined unit cell parameters in space group $P42_12$ (no. 90) are $a = b$ = 7.3719(13) Å, c = 10.6983(11) Å.

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