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Hydrothermal Synthesis, Crystal Structure, and Solid-State NMR Spectroscopy of a New Indium Silicate: $K_2In(OH)(Si_4O_{10})$

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A new indium(III) silicate, $K_2In(OH)(Si_4O_{10})$, has been synthesized by a high-temperature, high-pressure hydrothermal method. It crystallizes in the monoclinic space group $P2_1/m$ (No. 11) with $a = 11.410(1)$ Å, $b = 8.373(1)$ Å, $c = 11.611(1)$ Å, $\beta = 112.201(2)°$, and $Z = 4$. The structure, which is analogous to that of $K_2CuSi_4O_{10}$, consists of unbranched vierer 4-fold chains of corner-sharing SiO_4 tetrahedra running along the *b* axis linked together via corner sharing by chains of *trans*-corner-sharing $InO_4(OH)_2$ octahedra to form a 3-D framework which delimits 8-ring and 6-ring channels to accommodate K^+ cations. The presence of hydroxyl groups is confirmed by IR spectroscopy. The ^{29}Si MAS NMR exhibits four resonances at –88.6, –90.1, –97.4, and –98.2 ppm corresponding to four distinct crystallographic Si sites. A $^1H \rightarrow {}^{29}Si$ CP/MAS NMR experiment was performed to assign the four resonances.

Introduction

Open-framework phosphates of group 13 elements have been extensively researched because of their interesting structural chemistry and potential applications in catalysis.[1,2] Although some of the phosphates have extralarge rings in their structures, most of them have limited thermal stability that makes their use as molecular sieves difficult. This is in contrast to the high thermal stability and extensive applications of aluminosilicate zeolites in refinery and petrochemical processes. A large number of natural and synthetic zeolites have been reported. The properties of zeolites can be modified by substitution of framework aluminum and/or silicon by other tetrahedral atoms. The substitution of Al with Ga in known aluminosilicate frameworks has been extensively studied.[3] A novel gallosilicate having no counterpart among aluminosilicates has also been synthesized.[4] In contrast, much less work has been reported on the heavier group 13 silicates. Indium represents an interesting case since, by comparison with the smaller Al and Ga, which usually adopt 4-fold coordination, In is only expected to occur with octahedral coordination. Previously several indium silicates have been reported, $In_2Si_2O_7$ (pyrochlore),[5] $NaInSi_2O_6$ (pyroxene),[6] $Ca_3In_2Si_2O_6$ (garnet),[7] $Pb_2In_2Si_2O_9$,[8] which consists of zigzag infinite chains of edge-sharing InO_6 octahedra connected by Si_2O_7 double tetrahedra, and a family of microporous indium silicate compositions with unknown crystal structures.[9] Because we have been interested in the exploratory synthesis of mixed octahedral−tetrahedral framework oxides, we therefore extended the search for new materials into the system of metal silicates. Our synthetic methods are 2-fold, namely, mild hydrothermal reactions in Teflon-lined autoclaves at 100−200 °C using organic amines as templates and high-temperature, high-pressure hydrothermal reactions in gold ampules contained in a high-pressure reaction vessel at 500−600 °C using alkali-metal cations as

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templates. Recently, a number of vanadosilicates,[10] three uranium silicates,[11] and one organically templated niobium silicate[12] were reported by Jacobson and co-workers. We synthesized a new vanadosilicate, $Rb_2(VO)(Si_4O_{10})\cdot xH_2O$,[13] which has the same framework stoichiometry as $K_2(VO)(Si_4O_{10})\cdot H_2O$ and the mineral $Ca(VO)(Si_4O_{10})\cdot 4H_2O$,[14,15] but it adopts a considerably different structure. We also reported the first example of two-bond *J*-coupling between a quadrupolar nucleus and a spin 1/2 nucleus in the solid state during the NMR study of the new niobium silicate $Rb_4(NbO)_2(Si_8O_{21})$.[16] In this paper, we report the synthesis, crystal structure, and solid-state NMR spectroscopy of $K_2In(OH)(Si_4O_{10})$, denoted as **1**. The framework structure of this new indium silicate, which is analogous to that of $K_2CuSi_4O_{10}$,[17] consists of chains of *trans*-corner-sharing $InO_4(OH)_2$ octahedra and 8-ring channels formed by unbranched vierer 4-fold silicate chains. This is the first example of hydrothermal synthesis of indium silicate under high temperature and high pressure.

Experimental Section

Synthesis and Characterization. Compound **1** was obtained from a high-temperature, high-pressure hydrothermal reaction in a gold ampule contained in a Leco Tem-Pres autoclave where pressure was provided by water. The degree of filling of the autoclave by water at room temperature is 55%. A reaction mixture of KOH_{aq}, In_2O_3, and SiO_2 (molar ratio K:In:Si = 4:1:4) in a 4.7 cm long gold ampule (inside diameter 4.85 mm) was heated at 600 °C for 2 d. The pressure was estimated to be 170 MPa according to the pressure−temperature diagram of pure water. The autoclave was then cooled to 350 °C at 5 °C/h followed by fast cooling to room temperature by turning off the power of the tube furnace. The product contained colorless rod crystals and powder. A colorless rod crystal was selected for single-crystal X-ray diffraction study. The product was a single phase of **1** as indicated from a comparison of the X-ray powder pattern of the bulk product to the pattern simulated from the atomic coordinates derived from the single-crystal study. The powder pattern differs from those of the microporous indium silicate compositions reported by Bedard et al.[9] The yield was 68% based on indium. The sample was used for IR and solid-state NMR spectroscopy study.

Single-Crystal X-ray Diffraction. A colorless crystal of dimensions 0.08 × 0.08 × 0.1 mm^3 was selected for indexing and intensity data collection on a Siemens Smart CCD diffractometer equipped with a normal focus, 3 kW sealed tube X-ray source. Intensity data were collected in 1271 frames with increasing ω (width of 0.3° per frame). The number of observed unique reflections ($F_o > 4\sigma(F_o)$) is 2442 ($2\theta_{max} = 56.52°$, $R_{int} = 0.039$). Empirical absorption corrections based on symmetry equivalents were performed by using the SADABS program for the Siemens area detector ($T_{min,max} = 0.914, 0.974$).[18] On the basis of systematic absences, statistics of intensity distribution, and successful solution and refinement of the structure, the space group was determined to be $P2_1/m$ (No. 11). The structure was solved by direct methods: The metal and Si atoms were first located, and the O and H atoms were found from difference Fourier maps. The final cycles of least-squares refinement including the atomic coordinates and anisotropic thermal parameters of all non-hydrogen atoms converged at R1 = 0.0508, wR2 = 0.1288, and $S = 1.321$. $\Delta\rho_{max,min} = 2.44, -1.23$ e·Å^{-3}. The largest residual electron density is at a distance of 0.88 Å from the indium atom. The atomic coordinates and isotropic thermal parameters of hydrogen atoms were fixed. Neutral-atom scattering factors were used for all the atoms. Anomalous dispersion and secondary extinction corrections were applied. All calculations were carried out with the PC version of the SHELXTL program package. The crystallographic data are given in Table 1, the atomic coordinates in Table 2, and bond lengths and bond valence sums in Table 3.[19]

Table 1. Crystallographic Data for $K_2In(OH)(Si_4O_{10})$

empirical formula	$HInK_2O_{11}Si_4$	space group	$P2_1/m$ (No. 11)
a/Å	11.410(1)	T/°C	23
b/Å	8.373(1)	λ(Mo Kα)/Å	0.71073
c/Å	11.611(1)	D_{calcd}/g·cm^{-3}	3.120
β/deg	112.201(2)	μ(Mo Kα)/cm^{-1}	36.3
V/Å^3	1027.0(2)	R1^a	0.0508
Z	4	wR2^b	0.1288
fw	482.39		

^{a} R1 = $\sum||F_o| - |F_c||/\sum|F_o|$. ^{b} wR2 = $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o,0) + 2(F_c)^2]/3$, where $a = 0.0231$ and $b = 22.0$.

Table 2. Atomic Coordinates and Thermal Parameters for $K_2In(OH)(Si_4O_{10})$

atom	x	y	z	U_{eq}^{a}
K(1)	0.5631(3)	0.25	0.9390(2)	0.0198(5)
K(2)	0.0829(3)	0.25	0.5830(2)	0.0192(5)
K(3)	0.4703(3)	0.25	0.5394(3)	0.0247(6)
K(4)	−0.0109(4)	0.25	−0.0266(3)	0.0414(9)
In(1)	0.28681(5)	0.00434(6)	0.21374(4)	0.0087(2)
Si(1)	0.2225(2)	−0.0636(2)	0.4699(2)	0.0102(4)
Si(2)	0.0094(2)	0.0688(2)	0.2547(2)	0.0098(4)
Si(3)	0.2498(2)	0.0629(2)	−0.1028(2)	0.0092(4)
Si(4)	0.3922(2)	−0.0588(2)	−0.2631(2)	0.0085(4)
O(1)	0.2705(5)	−0.0035(8)	0.6139(5)	0.017(1)
O(2)	0.3226(5)	−0.0324(7)	0.4096(5)	0.016(1)
O(3)	0.0889(5)	0.0341(7)	0.4025(5)	0.014(1)
O(4)	0.1792(8)	−0.25	0.4633(8)	0.018(2)
O(5)	0.0902(5)	0.0390(7)	0.1722(5)	0.015(1)
O(6)	−0.0461(7)	0.25	0.2442(7)	0.014(2)
O(7)	−0.1120(5)	−0.0500(7)	0.2171(5)	0.014(1)
O(8)	0.2471(6)	−0.0088(9)	0.0206(5)	0.022(1)
O(9)	0.2911(8)	0.25	−0.0951(9)	0.023(2)
O(10)	0.3544(5)	−0.0294(7)	−0.1428(5)	0.015(1)
O(11)	0.4111(8)	−0.25	−0.2742(8)	0.017(2)
O(12)	0.5159(5)	0.0340(6)	−0.2524(5)	0.013(1)
O(13)	0.3304(8)	0.25	0.2438(9)	0.020(2)
O(14)	0.2560(9)	−0.25	0.205(1)	0.025(2)
H(13O)^b	0.4260	0.25	0.2573	0.05
H(14O)^b	0.2333	−0.25	0.2793	0.05

^{a} U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor. ^{b} The atomic coordinates and isotropic thermal parameters of hydrogen atoms are fixed.

IR and Solid-State NMR Measurements. The IR spectrum was recorded within the 500−4000 cm^{-1} region on a BIO-RAD FTS

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Table 3. Bond Lengths (Å) and Bond Valence Sums (Σ) for $K_2In(OH)(Si_4O_{10})$

K(1)−O(12)	2.756(6) (2×)	K(1)−O(8)	2.866(6) (2×)
K(1)−O(10)	2.867(7) (2×)	K(1)−O(9)	2.98(1)
K(1)−O(14)	3.10(1)	K(1)−O(10)	3.215(6) (2×)
	Σ[K(1)−O] = 1.20		
K(2)−O(7)	2.778(6) (2×)	K(2)−O(3)	2.788(6) (2×)
K(2)−O(4)	2.832(9)	K(2)−O(1)	2.938(6) (2×)
K(2)−O(3)	3.127(6) (2×)		
	Σ[K(2)−O] = 1.20		
K(3)−O(2)	2.863(6) (2×)	K(3)−O(12)	2.904(6) (2×)
K(3)−O(2)	2.963(6) (2×)	K(3)−O(13)	3.19(1)
	Σ[K(3)−O] = 0.80		
K(4)−O(14)	2.78(1)	K(4)−O(5)	2.788(6) (2×)
K(4)−O(5)	2.894(6) (2×)	K(4)−O(6)	3.318(9)
	Σ[K(4)−O] = 0.81		
In(1)−O(13)	2.114(2)	In(1)−O(8)	2.116(6)
In(1)−O(5)	2.129(5)	In(1)−O(12)	2.146(5)
In(1)−O(14)	2.155(2)	In(1)−O(2)	2.175(5)
	Σ[In(1)−O] = 3.17		
Si(1)−O(2)	1.571(6)	Si(1)−O(1)	1.630(5)
Si(1)−O(4)	1.630(3)	Si(1)−O(3)	1.645(6)
	Σ[Si(1)−O] = 4.05		
Si(2)−O(5)	1.580(6)	Si(2)−O(7)	1.625(6)
Si(2)−O(6)	1.630(4)	Si(2)−O(3)	1.636(5)
	Σ[Si(2)−O] = 4.05		
Si(3)−O(8)	1.564(6)	Si(3)−O(9)	1.628(3)
Si(3)−O(10)	1.630(6)	Si(3)−O(7)	1.633(6)
	Σ[Si(3)−O] = 4.13		
Si(4)−O(12)	1.575(6)	Si(4)−O(11)	1.627(2)
Si(4)−O(10)	1.629(5)	Si(4)−O(1)	1.638(6)
	Σ[Si(4)−O] = 4.08		
O(13)−H(13O)	1.04	O(14)−H(14O)	1.00

155 FTIR spectrometer using the mull technique. To a 10 mg ground sample was added two drops of Fluorolube. The mixture was ground and contained between two KBr plates for measurement.

^{29}Si magic angle spinning (MAS) NMR spectra were recorded on a Bruker AVANCE-400 spectrometer equipped with a double-tuned 4 mm MAS probe, with a resonance frequency of 79.46 MHz for the ^{29}Si nucleus. A $\pi/4$ pulse width of 2 μs and a repetition time of 10 s were used to acquire ^{29}Si MAS NMR spectra, which were Bloch decay spectra under conditions of no proton decoupling. The T_1 values were measured with an inversion−recovery pulse sequence. The Hartmann−Hahn condition for $^1H \rightarrow {}^{29}Si$ cross-polarization (CP) experiments was determined by using the cubic octamer silicic acid trimethylsilyl ester Q_8M_8. The optimal contact time for $^1H \rightarrow {}^{29}Si$ CP was found to be 3 ms, and a repetition time of 4 s was used. ^{29}Si chemical shifts were externally referenced to TMS at 0.0 ppm. Totals of 2464 and 18968 scans were accumulated for the ^{29}Si one-pulse and CP/MAS NMR spectra, respectively. A line broadening of 10 Hz was used to process the NMR data. The amount of sample in the rotor was about 55 mg.

Results and Discussion

Structure. As shown in Figure 1, the structure of **1** is constructed from the following structural elements: four SiO_4 tetrahedra, each with three corners shared with other tetrahedra, and the fourth corner coordinated to one In atom, one In atom coordinated to two OH^- groups and the apexes of four SiO_4 tetrahedra in octahedral coordination, and four K^+ ions. The structure consists of infinite tubular chains of corner-sharing SiO_4 tetrahedra running along the *b* axis linked together via corner sharing by infinite chains of $InO_4(OH)_2$ octahedra to form a 3-D framework which delimits 8-ring and 6-ring channels to accommodate K^+ cations (Figure 2a). The structure is analogous to that of the synthetic copper(II) silicate $K_2CuSi_4O_{10}$ which was also synthesized under hydrothermal conditions. The latter consists of the same type of tubular chains, which are connected by square planar CuO_4 groups.

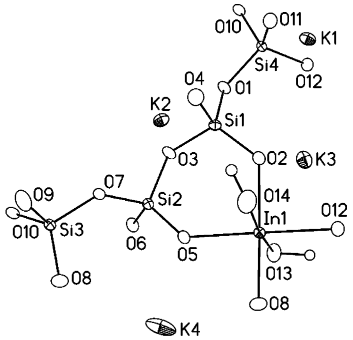

Figure 1. Building units of **1** showing atom labeling scheme. Thermal ellipsoids are shown at 50% probability. Small open circles are H atoms.

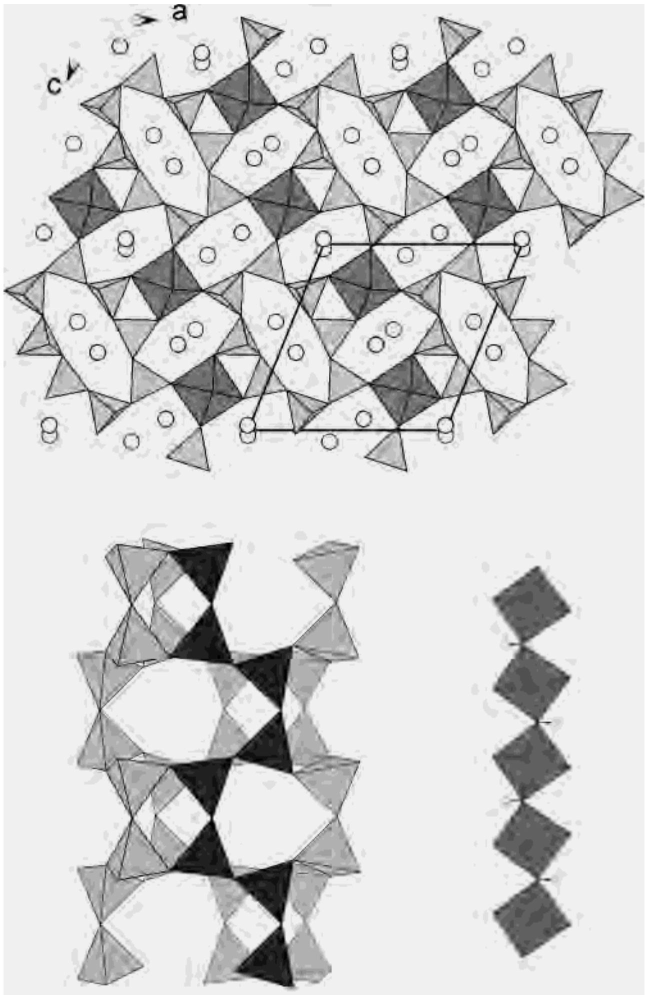

Figure 2. (a, top) Structure of **1** viewed along the *b* axis. The medium gray and light gray polyhedra are $InO_4(OH)_2$ octahedra and SiO_4 tetrahedra, respectively. Open circles are potassium atoms. H atoms are not shown. (b, bottom left) Section of an unbranched vierer 4-fold silicate chain in **1**. One of the fundamental chains defining the 4-fold chain is distinguished by dark gray tetrahedra. (c, bottom right) Section of an infinite chain of *trans*-corner-sharing $InO_4(OH)_2$ octahedra. The small open circles represent H atoms.

The tubular silicate chain can be constructed by condensation of an infinite number of unbranched 8-rings. The sequence of directedness within the 8-ring is UUDUDDUD, where U refers to a terminal oxygen corner pointing up and D to one pointing down. Adjacent 8-rings are symmetry related by a mirror plane. The tubular chain can also be constructed by condensation of four unbranched single chains with a periodicity of four. According to the classification of Liebau, this type of tubular chain is called an "unbranched vierer 4-fold chain" and can be described by the following structural formula: (uB, 4^1_∞)[$^4Si_{16}O_{40}$].[20] In Figure 2b, one of the fundamental chains defining the 4-fold chain is distinguished by dark tetrahedra. The $InO_4(OH)_2$ octahedron shares its equatorial plane corners with two U tetrahedra from two tubular chains and two UD tetrahedra from one chain. The 6-ring channel is formed by the edges of four SiO_4 tetrahedra from two tubular chains and two $InO_4(OH)_2$ octahedra. The framework structure contains single chains of *trans*-corner-sharing $InO_4(OH)_2$ octahedra isolated from each other by tubular silicate chains. The In metal atoms are linked together by means of single bridges of hydroxyl groups (Figure 2c). The hydrogen atom H(13O) is H-bonded with O(11), whereas the other hydrogen atom, H(14O), is not involved in hydrogen bonding. The $InO_4(OH)_2$ octahedron is quite regular as shown by the In−O bond distances ranging from 2.116 to 2.175 Å. There are two octahedra per chain of unit cell length along the *b* axis. Both hydroxyl groups lie in mirror planes. The silicate groups are slightly distorted with the Si−O bond distances ranging from 1.572 to 1.646 Å. The shortest distance in each silicate group corresponds to the oxygen atom bonded to indium. Each silicate group shares corners with three silicate groups and one $InO_4(OH)_2$ octahedron. The Si−O−In bond angles are 127.5°, 133.7°, 151.6°, and 141.3° for Si(1), Si(2), Si(3), and Si(4), respectively. All potassium atoms lie in mirror planes. K(2) is located in the 8-ring channels, whereas the other K atoms are located in the 6-ring channels. The coordination number of K is determined on the basis of the maximum gap in the K−O distances ranked in increasing order. The agreement with the maximum cation−anion distance suggested by Donnay and Allmann is also checked.[21] The K(1), K(2), K(3), and K(4) cations are coordinated by 10, 9, 7, and 6 oxygen atoms, respectively. K(1) and K(2) are observed from a comparison of their bond valence sums and thermal parameters with those for K(3) and K(4) to be more strongly bound.

IR and Solid-State NMR Spectroscopy. The IR spectrum shows two O−H stretching absorption bands at 3560 and 3506 cm^{-1} (Figure 3). The absorption at 3506 cm^{-1} can be assigned to O(13)−H(13O) because hydrogen bonding causes the O−H stretching absorption to appear at a lower wavenumber. The reason the intensity of the band at 3506 cm^{-1} is stronger than the other one can be ascribed to the decrease of the strength of the O(13)−H(13O) bond; hence, there is a larger change in the dipole moment during the vibration, so a greater intensity of the absorption band is associated with the vibration. The absorption bands in the region below 1500 cm^{-1} are from Fluorolube.

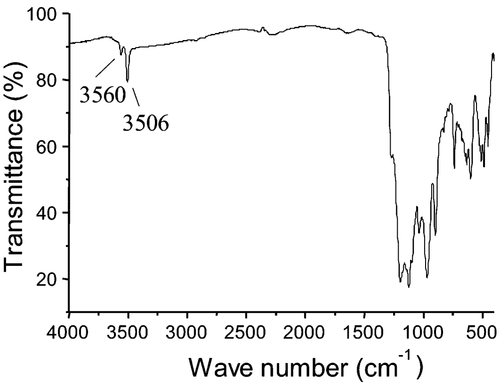

Figure 3. Infrared spectrum of **1** (Fluorolube mull).

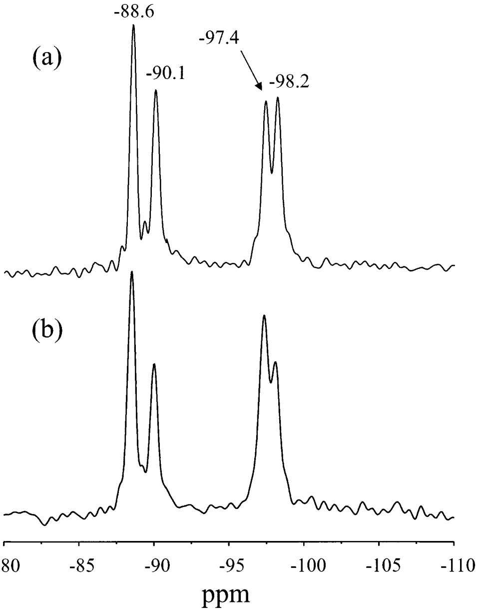

Figure 4. (a) ^{29}Si one-pulse and (b) $^1H \rightarrow {}^{29}Si$ CP/MAS NMR spectra of **1** acquired at a spinning speed of 12 kHz.

^{29}Si solid-state NMR is used to provide information on the local environments of silicon atoms in the framework. The ^{29}Si one-pulse and CP/MAS NMR spectra of **1** are shown in Figure 4. Four resonances, which can be divided into two subgroups at (−88.6, −90.1) and (−97.4, −98.2) ppm, are observed with nearly identical intensities, corresponding to four distinct silicon sites as determined from X-ray diffraction. As seen in Figure 4b, an enhancement in the signal intensity at −97.4 ppm is observed when ^1H to ^{29}Si CP is applied, indicating that this Si site is in close proximity to hydroxyl groups as compared to other Si sites. This observation also provides indirect evidence of the presence of hydroxyl groups in the structure, in good agreement with IR results. The resonance at −97.4 ppm can be assigned to Si(4) because OH(13O) is H-bonded with Si(4)O_4. In addition, the T_1 value, obtained with an inversion−recovery pulse sequence, for the Si(1) site is 170 s, and those for the other three Si sites are 220−230 s. The difference in the peak height ratio for Si(1)/Si(2) in Figure 4 is probably due to the T_1 difference and CP efficiency. The much larger

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difference for Si(4)/Si(3) is expected since the Si(4) signal is enhanced in the CP spectrum due to its higher CP efficiency.

It has been reported that the ^{29}Si chemical shift depends on the average value of the four Si−O−T bond angles (three Si−O−Si angles and one Si−O−In angle for each silicon) and shifts upfield with increasing Si−O−T bond angle.[22] One may assign NMR inequivalent silicon sites on the basis of X-ray diffraction analysis results. The average Si−O−T bond angles in **1** are 133.5°, 134.0°, 144.2°, and 143.1° for Si(1), Si(2), Si(3), and Si(4), respectively. The angles for the latter two Si atoms are considerably larger than those for the former two. The resonances at (−88.6, −90.1) and (−97.4, −98.2) ppm are therefore assigned to (Si(1), Si(2)) and (Si(4), Si(3)), respectively. This assignment is also consistent with ^{1}H → ^{29}Si CP/MAS NMR results.

In summary, we have synthesized a new indium silicate and characterized its structure by single-crystal X-ray diffraction and IR and solid-state NMR spectroscopies. The structure consists of unbranched vierer 4-fold silicate chains which are linked by chains of $InO_4(OH)_2$ octahedra into a 3-D framework containing 8-ring and 6-ring channels that are occupied by K^+ cations. This is the first example of hydrothermal synthesis of indium silicate under high temperature and high pressure. An isostructural vanadosilicate, $K_2(VO)(Si_4O_{10})$, has also been synthesized under a similar hydrothermal condition.[23] In contrast to the *VSH-n* phases which are based on silicate single layers, the title compound is based on tubular silicate chains. The extremely rich structural chemistry of metal silicates is evidenced by at least seven different structures with the composition $A_2(VO)(Si_4O_{10})\cdot nH_2O$ (A = alkali- or alkaline-earth-metal cation, $n \geq 0$). More interestingly, the topology and composition spectrum of the silicate structures may be greatly increased by using organic templates. The synthesis of a large number of new and interesting silicate materials with unique structures and properties is promising.

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Supporting Information Available: Crystallographic data for $K_2In(OH)(Si_4O_{10})$ in CIF format and experimental and simulated X-ray powder patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

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