Inorg. Chem. **2005**, *44*, 2992−2994

Inorganic Chemistry
Communication

$Rb_3In(H_2O)Si_5O_{13}$: A Novel Indium Silicate with a $CdSO_4$-Topological-Type Structure

Ling-I Hung,[†] Sue-Lein Wang,*[,†] Chia-Yi Chen,[‡] Bor-Chen Chang,[‡] and Kwang-Hwa Lii*[,‡,§]

Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 300, R.O.C.,
Department of Chemistry, National Central University, Chungli, Taiwan 320, R.O.C., and
Institute of Chemistry, Academia Sinica, Nankang, Taipei, Taiwan 115, R.O.C.

Received December 4, 2004

A novel indium silicate, $Rb_3In(H_2O)Si_5O_{13}$, has been synthesized using a high-temperature, high-pressure hydrothermal method and characterized by single-crystal X-ray diffraction. The structure consists of five-membered rings of corner-sharing SiO_4 tetrahedra connected via corner sharing to four adjacent five-membered rings to form a 3D silicate framework that belongs to the $CdSO_4$ topological type. The InO_6 octahedron shares five of its corners with five different SiO_4 tetrahedra to form a 3D framework that delimits two types of channels to accommodate the rubidium cations. The sixth corner of InO_6 is coordinated H_2O. The structure is related to that of the titanium silicate ETS-10, and these are the only two metal silicates that have the $CdSO_4$-topological-type structure. In addition, the crystal of $Rb_3In(H_2O)Si_5O_{13}$ shows an intense second harmonic generation signal. Crystal data: $H_2Rb_3InSi_5O_{14}$, monoclinic, space group *Cc* (No. 9), $a = 9.0697(5)$ Å, $b = 11.5456(6)$ Å, $c = 13.9266(8)$ Å, $\beta = 102.300(1)°$, $V = 1424.8(1)$ Å^3, and $Z = 4$.

Recently, much work has focused on the synthesis of metal silicates because of their interesting structural chemistry and generally greater thermal stability than the corresponding phosphates. A good number of vanadium silicates have been synthesized.[1−4] Some of them show good thermal stability, absorption, and ion-exchange properties, suggesting their potential for applications as molecular sieves or in catalysis. A series of uranium silicates has also been developed by replacing the VO^{2+} cation in the vanadium(IV) silicates with UO_2^{2+} as the bridging metal species.[5−7] Other recent examples include titanium,[8,9] niobium,[10,11] cerium,[12,13] tin,[14] and indium[15,16] silicates. Most of these compounds were synthesized with alkali metal cations under hydrothermal conditions at 180−240 °C. A uranium silicate and a niobium silicate have been synthesized by using organic ammonium templates.[6,10] We have also synthesized a number of new silicates of V, Nb, and In by high-temperature, high-pressure hydrothermal reactions in gold ampules using alkali metal cations.[4,11,15,16] For example, we reported the synthesis of $Rb_4(NbO)_2Si_8O_{21}$ and its solid-state NMR spectra.[11] The ^{29}Si MAS NMR spectrum shows multiplet patterns that arise from ^{93}Nb (spin-$^9/_2$)−^{29}Si *J* coupling. This is the first example of two-bond *J* coupling between a quadrupolar nucleus and a spin-$^1/_2$ nucleus in the solid state. The framework structure of $K_2In(OH)Si_4O_{10}$, which is analogous to that of $K_2CuSi_4O_{10}$, consists of chains of trans-corner-sharing $InO_4(OH)_2$ octahedra and 8-ring channels formed by unbranched vierer 4-fold silicate chains.[15] $Na_5InSi_4O_{12}$ consists of 12-membered single rings of silicate tetrahedra. The solid-state NMR spectroscopy and ionic conductivity have also been studied.[16] In this contribution, we report a new indium silicate with a 3D $CdSO_4$-topological-type structure[17] that is closely related to the well-known titano-

---

* To whom correspondence should be addressed. E-mail: liikh@cc.ncu.edu.tw (K.-H.L.).

[†] National Tsing Hua University.

[‡] National Central University.

[§] Academia Sinica.

(1) Wang, X.; Liu, L.; Jacobson, A. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 2174.
(2) Wang, X.; Liu, L.; Jacobson, A. J. *J. Am. Chem. Soc.* **2002**, *124*, 7812.
(3) Huang, J.; Wang, X.; Liu, L.; Jacobson, A. J. *Solid State Sci.* **2002**, *4*, 1193.
(4) Li, C.-Y.; Hsieh, C.-Y.; Lin, H.-M.; Kao, H.-M.; Lii, K.-H. *Inorg. Chem.* **2002**, *41*, 4206.
(5) Wang, X.; Huang, J.; Liu, L.; Jacobson, A. J. *J. Mater. Chem.* **2002**, *12*, 406.
(6) Wang, X.; Huang, J.; Jacobson, A. J. *J. Am. Chem. Soc.* **2002**, *124*, 15190.
(7) Huang, J.; Wang, X.; Jacobson, A. J. *J. Mater. Chem.* **2003**, *13*, 191.
(8) Nyman, M.; Bonhomme, F.; Teter, D. M.; Maxwell, R. S.; Gu, B. X.; Wang, L. M.; Ewing, R. C.; Nenoff, T. M. *Chem. Mater.* **2000**, *12*, 3449.
(9) Nyman, M.; Bonhomme, F.; Maxwell, R. S.; Nenoff, T. M. *Chem. Mater.* **2001**, *13*, 4603.
(10) Francis, R. J.; Jacobson, A. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 2879.
(11) Kao, H.-M.; Lii, K.-H. *Inorg. Chem.* **2002**, *41*, 5644.
(12) Rocha, J.; Ferreira, P.; Carlos, L. D.; Ferreira, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3276.
(13) Jeong, H.-K.; Chandrasekaran, A.; Tsapatsis, M. *Chem. Commun.* **2002**, 2398.
(14) Ferreira, A.; Lin, Z.; Rocha, J.; Morais, C. M.; Lopes, M.; Fernandez, C. *Inorg. Chem.* **2001**, *40*, 3330.
(15) Hung, L.-I.; Wang, S.-L.; Kao, H.-M.; Lii, K.-H. *Inorg. Chem.* **2003**, *42*, 4057.
(16) Hung, L.-I.; Wang, S.-L.; Szu, S.-P.; Hsieh, C.-Y.; Kao, H.-M.; Lii, K.-H. *Chem. Mater.* **2004**, *16*, 1660.

10.1021/ic048296n CCC: $30.25

silicate ETS-10.[18,19] It crystallizes in a noncentrosymmetric space group and has an intense SHG (second harmonic generation) signal.

$Rb_3In(H_2O)Si_5O_{13}$ (denoted as **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 apparatus is an externally heated cold-seal pressure vessel for use to 10000 bar and 750 °C.[20] A reaction mixture of 1.33 mL of $RbOH_{(aq)}$ (Aldrich, 50 wt %), 0.360 g of In_2O_3 (Cerac, 99.99%), and 0.468 g of SiO_2 (Alfa Aesar, 99.995%) (Rb/In/Si molar ratio = 4.36:1:3) was loaded in a 6.0-cm-long gold ampule with an i.d. of 9.6 mm. The open end of the ampule was crimped, hammered flat, and then welded with a torch. The sealed ampule was then placed in the autoclave and counter-pressured with water at a fill level of 55%. The autoclave was heated at 600 °C for 8 h, cooled to 350 °C at 5 °C/h, and then rapidly cooled to room temperature by turning off the power of the tube furnace. The pressure at 600 °C was estimated to be 170 MPa according to the pressure−temperature diagram of pure water. The product contained colorless crystals of **1** in a yield of about 40% based on SiO_2 and yellow powder of excess In_2O_3. Some of the crystals were nearly 1 mm in each dimension. A small colorless crystal was selected for structure determination by single-crystal X-ray diffraction.[21] The large size of the crystals allowed for hand sorting of enough sample for further meansurements. The TGA curve showed a gradual weight loss of 2.4% in the range of 400−900 °C, which is close to the value of 2.44% calculated for the loss of the coordinated water molecule (see Figure S1 in the Supporting Information). A crystal with well-developed faces of dimensions 0.9 × 0.75 × 0.5 mm^3 was contained in a glass capillary for SHG measurement, and its signal was compared with that from a KH_2PO_4 (KDP) crystal of about the same size. The optimum reaction conditions for a pure product of **1** have not been found. We also carried out reactions at 600 °C for a longer heating time (72 h) or using different ratios of starting materials; the major products were either $Rb_2In(OH)Si_4O_{10}$, which is isostructural with $K_2In(OH)Si_4O_{10}$,[15] or the new phase $Rb_5In_3Si_7O_{21}$.[22]

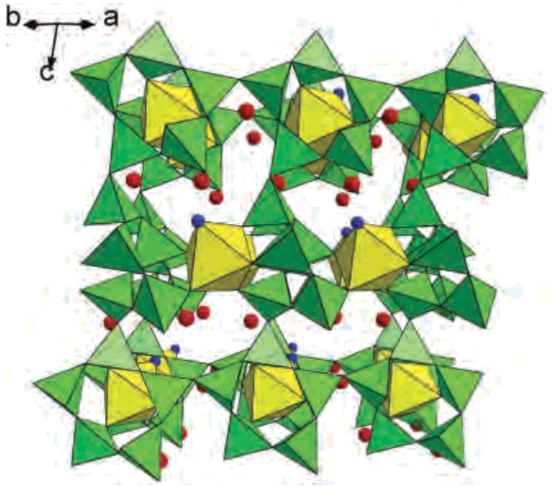

Figure 1. Structure of **1** viewed along the [110] direction. The yellow and green polyhedra represent $InO_5(H_2O)$ octahedra and SiO_4 tetrahedra, respectively. Red and blue circles represent rubidium and water oxygen atoms, respectively.

The structure of **1** consists of five-membered puckered rings of corner-sharing SiO_4 tetrahedra. Each 5-ring shares two corners with adjacent 5-rings to form parallel infinite chains along [110] and $[\bar{1}10]$ directions. The chains are packed into layers parallel to the (001) plane with the chains in neighboring layers perpendicular to each other. Each 5-ring in a chain is connected via corner-sharing with two 5-rings in neighboring layers to form a 3D silicate framework that belongs to the $CdSO_4$ topological type. One corner of each 5-ring is unshared. The InO_6 octahedron shares five of its corners with five different SiO_4 tetrahedra belonging to two disconnected 5-rings to form a 3D framework that delimits two types of channels to accommodate the rubidium cations (Figure 1). The sixth corner of InO_6 is coordinated H_2O, which is H-bonded to O(8), the terminal oxygen on $Si(3)O_4$ [$O(14)-H(2)\cdots O(8) = 1.91$ Å, $\angle O(14)-H(2)-O(8) = 130.4°$]. The InO_6 octahedron is quite regular as shown by the In−O distances ranging from 2.133 to 2.171 Å with an average value of 2.155 Å, which is in accord with the sum of effective ionic radii for $^{IV}O^{2-}$ and $^{VI}In^{3+}$ according to Shannon.[23] Atom In(1) is displaced from the centroid of its In−O octahedron by only 0.045 Å. The octahedral distortion can be estimated by using the equation $\Delta = {}^1/_6\sum[(R_i - R_{av})/R_{av}]^2$, where R_i is the individual bond length and R_{av} is the average bond length.[23] The calculation gives $\Delta = 4.4 \times 10^{-5}$, which is comparable with the value for $In(1)O_6$ of $RbIn(OH)PO_4$ and $NH_4In(OH)PO_4$.[24,25] The observed Si−O bond lengths (1.579−1.642 Å) and O−Si−O bond angles (100.7−115.8°) are typical values and are within the normal range.[26] The shortest distance in each silicate group corresponds to the oxygen atom bonded to indium. $Si(1)O_4$, $Si(2)O_4$, $Si(4)O_4$, and $Si(5)O_4$ each shares corners with three silicate groups and one InO_6 octahedron, whereas $Si(3)O_4$ has one

---

(17) O'Keeffe, M. *Z. Kristallogr.* **1991**, *196*, 21.

(18) Wang, X.; Jacobson, A. J. *Chem. Commun.* **1999**, 973.

(19) Anderson, M. W.; Terasaki, O.; Ohsuna, T.; Malley, P. J. O.; Philippou, A.; Mackay, S. P.; Ferreira, A.; Rocha, J.; Lidin, S. *Nature* **1994**, *367*, 347.

(20) Luth, W. C.; Tuttle, O. F. *Am. Mineral.* **1963**, *48*, 1401.

(21) Crystal data for **1**: $H_2Rb_3InSi_5O_{14}$, colorless tabular crystal of dimensions 0.2 × 0.1 × 0.1 mm, $T = 293$ K, monoclinic, space group *Cc* (No. 9), $a = 9.0697(5)$ Å, $b = 11.5456(6)$ Å, $c = 13.9266(8)$ Å, $\beta = 102.300(1)°$, $V = 1424.8(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 3.439$ g cm^{-3}, $\lambda = 0.71073$ Å, $\mu = 12.334$ mm^{-1}, 4937 reflections measured, 2551 unique reflections with $I > 2\sigma(I)$ ($2\theta_{max} = 56.6°$, $R_{int} = 0.0313$), GOF = 1.045, R1 = 0.0209, wR2 = 0.0522. The H atoms of the coordinated water were located from the difference Fourier maps. The final cycles of least-squares refinement included atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms. The atomic coordinates and isotropic thermal parameters for H atoms were fixed.

(22) Crystal data for $Rb_5In_3Si_7O_{21}$: orthorhombic, $Pna2_1$, $a = 12.6338(6)$ Å, $b = 17.0778(8)$ Å, $c = 10.3376(5)$ Å, and R1 = 0.041. The 3D framework structure consists of siebener single chains of corner-sharing SiO_4 tetrahedra, InO_5 trigonal bipyramids, and face-sharing octahedral dimers with the composition In_2O_9.

(23) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

(24) Lii, K.-H. *J. Chem. Soc., Dalton Trans.* **1996**, 815.

(25) Filaretov, A. A.; Zhizhin, M. G.; Komissarova, L. N.; Danilov, V. P.; Chernyshev, V. V.; Lazoryak, B. I. *J. Solid State Chem.* **2002**, *166*, 362.

(26) Liebau, F. *Structural Chemistry of Silicates: Structure, Bonding and Classification*; Springer-Verlag: Berlin, 1985.

terminal oxygen. The Si$-$O$_{br}-$Si bond angles are in the range from 131.2° to 162.4°.

The rubidium cations that are located in the cavities within the framework occupy three nonequivalent sites. Using the maximum cation$-$anion distance of Donnay and Allmann,[27] a limit of 3.44 Å was set for Rb$-$O interactions, which gives the following coordination numbers: Rb(1) and Rb(3), 8-coordinate; Rb(2), 10-coordinate. The bond-valence sums for all Rb cations are close to 1.

The structure of **1** is related to that of the well-known titanium silicate ETS-10, $Na_2TiOSi_5O_{12}\cdot xH_2O$. ETS-10 crystallizes in a centrosymmetric tetragonal space group, and the structure consists of infinite chains of trans-corner-sharing TiO_6 octahedra. Each titanium octahedron is surrounded by four silicate tetrahedra to form $[TiSi_4O_{13}]$ columns that are connected by additional silicate tetrahedra to form a 3D framework structure with 12-ring channels. The silicate tetrahedra in ETS-10 are also connected together in 5-rings that share edges with two adjacent 5-rings to form infinite silicate chains along the [100] direction (Figure 2). The chains are packed into layers parallel to the (001) plane with the chains in neighboring layers perpendicular to each other. Each 5-ring in a chain is connected via corner sharing with a 5-ring in a neighboring layer to form a 3D $CdSO_4$-topological-type silicate framework. To our knowledge, ETS-10 and compound **1** are the only two examples in the area of metal silicates that can be ascribed to the $CdSO_4$ topological type. In contrast to ETS-10, the 5-rings in **1** are connected by corner sharing only. Both silicate networks consist of wide channels. In ETS-10, neighboring channel positions cannot be simultaneously occupied by $TiO_4O_{2/2}$ chains. The unoccupied positions correspond to 12-ring channels. In the structure of **1**, all channels are occupied by discrete $InO_5(H_2O)$ octahedra such that two types of smaller channels are formed.

$Rb_3In(H_2O)Si_5O_{13}$ crystallizes in a noncentrosymmetric space group, *Cc*. Because SHG provides a highly sensitive and definitive test of the absence of a center of symmetry of crystalline materials, the SHG response of crystals of **1** was measured. When the crystal was exposed to the fundamental output (1064 nm) of a pulsed Nd:YAG laser, a green emission generated from this crystal could be seen with the naked eye, which is indicative of intense SHG. A small portion (<10 mJ/pulse) of the Nd:YAG laser 1064-nm output was aligned to pass through the crystal, and the SHG signal at 532 nm was imaged onto a monochromator attached to an intensified charge-coupled device (ICCD) detector. The SHG signal was detected by the ICCD detector and was then recorded on a personal computer. In the SHG measurements, the orientations of both the $Rb_3In(H_2O)Si_5O_{13}$ crystal and the KDP crystal were optimized for the maximum SHG signal. Consequently, the measurements show that the SHG efficiency for the $Rb_3In(H_2O)Si_5O_{13}$ crystal is at least approximately 10% of that for the KDP crystal (See Figure S2 in the Supporting Information). It is unclear to us why compound **1** shows a much more intense SHG signal than $RbIn(OH)PO_4$ and $NH_4In(OH)PO_4$, even though the distortions of InO_6 octahedra in these three structures are comparable.

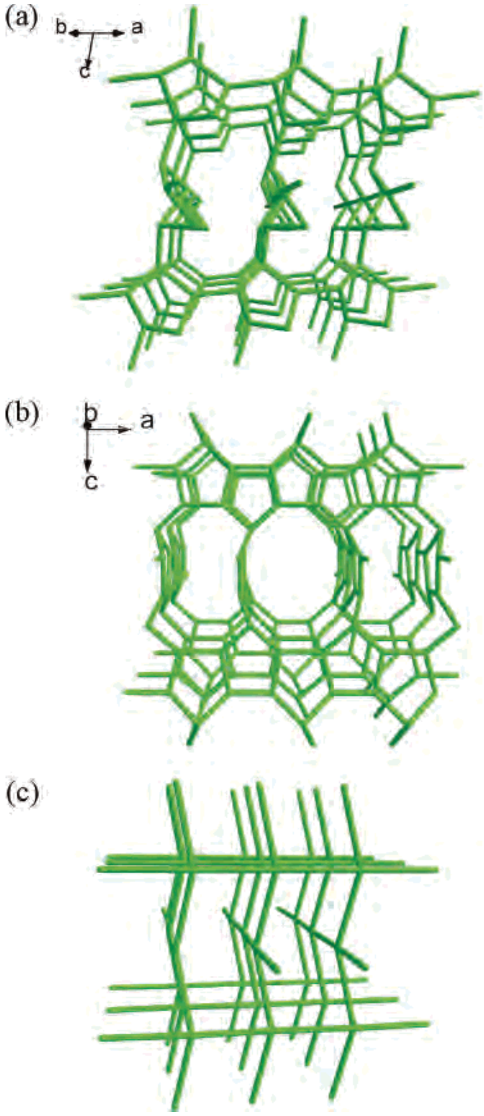

Figure 2. (a) Silicate framework of **1** viewed along the [110] direction. The silicate 5-rings are connected by sharing corners. (b) Silicate framework of ETS-10 viewed along [010] direction. The 5-rings share edges and corners. (c) Network structure of $CdSO_4$. In these simplified schematic diagrams, a tetrahedral atom is located at the intersection of the lines, as oxygen bridges are made by corner sharing from the vertices of the tetrahedron.

In summary, this work demonstrates that a novel 3D indium silicate was synthesized under high-temperature, high-pressure hydrothermal conditions. The compound is unique in that, among the vast number of synthetic silicates and naturally occurring silicate minerals, it and the titanium silicate ETS-10 are the only two examples in which the silicate frameworks adopt the $CdSO_4$ topological type. The crystal of the title compound shows an intense SHG signal.

Acknowledgment. We thank the National Science Council of Taiwan for support.

Supporting Information Available: Crystallographic data for **1** in CIF format, TGA curve, and SHG measurement results. This material is available free of charge via the Internet at http://pubs.acs.org.

IC048296N

---

(27) Donnay, G.; Allmann, R. *Am. Mineral.* **1970**, *55*, 1003.