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Article

$Rb_6(InCo)_2(Si_9O_{26})$: A Mixed-Metal Silicate Containing 20-Membered-Ring Silicate Single Layers with a Very Low Si:O Ratio

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A new cobalt–indium silicate, $Rb_6(InCo)_2(Si_9O_{26})$, has been synthesized via a high-temperature, high-pressure hydrothermal method and characterized by single-crystal X-ray diffraction. It crystallizes in the noncentrosymmetric orthorhombic space group *Aba*2 (No. 41) with $a = 20.779(1)$ Å, $b = 12.0944(6)$ Å, $c = 10.7761(5)$ Å, $V = 2708.1(2)$ Å^3, and $Z = 4$. The structure consists of 20-membered-ring silicate single layers of corner-sharing SiO_4 tetrahedra interconnected by dimers of edge-sharing CoO_4 tetrahedra and InO_6 octahedra into a 3D framework. The Si:O ratio for the title compound is the lowest among the known single-layer silicates. Magnetic susceptibility confirms the divalent state of the cobalt ion. The powder sample has a second-harmonic-generation signal, confirming the absence of a center of symmetry in the structure.

Introduction

Aluminosilicate zeolites represent an important class of molecular sieves. The properties and structural diversities of zeolites can be modified by the substitution of framework aluminum by other tetrahedral atoms. The substitution of aluminum with gallium in known aluminosilicate frameworks has been extensively studied.[1] Two gallosilicates, TsG-1 and ECR-34, having no counterparts among aluminosilicates have also been synthesized.[2,3] In contrast, much less work has been reported on the heavier group 13 silicates. Indium presents an interesting case because, by comparison with the smaller aluminum and gallium, which usually adopt four-fold coordination, indium is expected to occur with octahedral coordination. We have recently synthesized several indium silicates via a high-temperature, high-pressure hydrothermal method (ca. 600 °C and 170 MPa).[4−6] All adopt nanoporous framework structures containing dissimilar silicate structure types such as 12-membered single rings, unbranched vierer four-fold chains, and 3D frameworks belonging to the $CdSO_4$ topological type.

The incorporation of transition metals into microporous aluminosilicates and aluminophosphates can lead to the modification of the physical and chemical properties of the parent compounds.[7−9] Cobalt(II) is one of the few transition-metal cations that easily exhibit tetrahedral coordination in addition to five- and six-fold coordination. This property has led to Co^{2+}-doped microporous solids by isomorphous substitution of framework constituents. It is expected that new framework structures can be prepared by incorporating Co^{2+} ions into indium silicate frameworks because the two metal cations usually adopt different coordinations. The results presented here concern the synthesis and characterization of a mixed-metal silicate, $Rb_6(InCo)_2(Si_9O_{26})$ (denoted as **1**), which consists of 20-membered-ring silicate single layers interconnected by dimers of edge-sharing InO_6 and CoO_4. To our knowledge, the Si:O ratio of the silicate layer is the lowest among the known single-layer silicates.

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Experimental Section

Synthesis and Characterization. High-temperature, high-pressure hydrothermal synthesis was performed in gold ampules 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 10 000 bar and 750 °C. A reaction mixture of 372 μL of RbOH(aq) (Aldrich, 50 wt %), 83 mg of In_2O_3 (Cerac, 99.8%), 37 mg of $Co(OH)_2$ (Strem, 97%), and 169 mg of SiO_2 (Alfa Aesar, 99.995%) (molar ratio Rb:In:Co:Si = 7.9:1.5:1:7) was placed in a 6.5-cm-long gold ampule with an i.d. of 4.8 mm. The sealed ampule was then put into the autoclave and counterpressured 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^{-1}, and then rapidly cooled to room temperature by turning off the power of the tube furnace. The pressure was estimated to be 170 MPa according to the pressure−temperature diagram of pure water. The product contained green chunk crystals of **1** and a small amount of colorless rod crystals of $Rb_2In(OH)Si_4O_{10}$, which is isostructural with $K_2In(OH)Si_4O_{10}$.[4] The crystals were easily separated by hand sorting, and the yield of **1** was estimated to be 46% based on $Co(OH)_2$. We have not been able to prepare a single phase of **1** despite many attempts, and the product was always contaminated with $Rb_2In(OH)Si_4O_{10}$. A suitable crystal of **1** was selected for single-crystal X-ray diffraction study. The In:Co ratio determined from single-crystal structure analysis was further confirmed by electron probe microanalysis. The purity of the sample for physical property measurements was confirmed by powder X-ray diffraction (Figure S1 in the Supporting Information).

Single-Crystal X-ray Diffraction. A green crystal of dimensions 0.1 × 0.1 × 0.1 mm^3 was selected for indexing and intensity data collection on a Bruker APEX diffractometer equipped with a normal-focus, 2-kW sealed-tube X-ray source. Intensity data were collected at room temperature in 1315 frames with ω scans (width of 0.30° per frame). Empirical absorption corrections based on symmetry equivalents were applied ($T_{min/max} = 0.546/0.974$). On the basis of reflection conditions, statistical analysis of the intensity distributions, and successful solution and refinement of the structures, the space group was determined to be *Aba*2 (No. 41). The structure was solved by direct methods and difference Fourier syntheses. The final cycles of least-squares refinement including atomic coordinates and anisotropic thermal parameters for all atoms converged at R1 = 0.0216, wR2 = 0.0464, and $S = 0.962$. The Flack x parameter was −0.014(5), indicative of a correct absolute structure. The final difference electron density maps were featureless, and the highest peak and deepest hole were +0.73 and −0.56 e·Å^{-3}. All calculations were performed using *SHELXTL*, version 5.1, software package.[10] The crystal data and structure refinement parameters are given in Table 1 and selected bond distances and bond valence sums in Table 2.[11]

Magnetic Susceptibility Measurements. Variable-temperature magnetic susceptibility $\chi(T)$ data were obtained on 71.8 mg of a polycrystalline sample of **1** from 2 to 300 K in a magnetic field of 5 kG after zero-field cooling using a Quantum Design SQUID magnetometer. Correction for diamagnetism was made according to Selwood.[12]

Second-Harmonic-Generation (SHG) Measurements. Compound **1** crystallizes in a noncentrosymmetric space group, *Aba*2. Because SHG provides a highly sensitive and definite test of the absence of a center of symmetry of crystalline materials, the SHG response of a powder sample of **1** was measured.[13] The experimental setup mainly consists of a Nd:YAG passively Q-switched laser of wavelength 1.064 μm as the fundamental pump source, a $^1/_2$-m, 0.3-nm-resolution grating monochromator as the spectral analyzer, and a photomultiplier tube as the signal detector. The Q-switched laser has a peak power of ~100 kW with a pulse width of ~0.5 ns and a repetition rate of 1 kHz. The sample powder was ungraded and loaded into a thin (~0.5-mm) cuvette.

Table 1. Crystallographic Data for $Rb_6(InCo)_2(Si_9O_{26})$

emperical formula	$Co_2In_2O_{26}Rb_6Si_9$
fw	1529.063
space group	*Aba*2 (No. 41)
a/Å	20.779(1)
b/Å	12.0944(6)
c/Å	10.7761(5)
V/Å^3	2708.1(2)
Z	4
T, °C	23
λ(Mo Kα), Å	0.71073
D_{calc}, g·cm^{-3}	3.750
μ(Mo Kα), mm^{-1}	14.108
R1^a	0.0216
wR2^b	0.0464

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o,0) + 2(F_c)^2]/3$, in which $a = 0.022$ and $b = 0$.

Table 2. Bond Lengths (Å) and Bond Valence Sums ($\sum s$) for **1**

Rb1−O10	2.810(3)	Rb1−O7	2.997(3)
Rb1−O1	3.076(3)	Rb1−O6	3.101(3)
Rb1−O3	3.173(3)	Rb1−O11	3.217(3)
Rb1−O5	3.251(3)	Rb1−O4	3.348(3)
Rb1−O13	3.428(3)		
$\sum s$[Rb1−O] = 0.91			
Rb2−O1	2.924(3) (2×)	Rb2−O3	2.938(3) (2×)
Rb2−O4	3.291(3) (2×)	Rb2−O13	3.344(3) (2×)
Rb2−O5	3.407(3) (2×)		
$\sum s$[Rb2−O] = 0.98			
Rb3−O8	2.873(3)	Rb3−O12	2.982(3)
Rb3−O10	2.996(3)	Rb3−O2	3.004(3)
Rb3−O11	3.072(3)	Rb3−O7	3.095(3)
Rb3−O1	3.120(3)	Rb3−O6	3.134(3)
$\sum s$[Rb3−O] = 1.02			
Rb4−O2	2.978(3) (2×)	Rb4−O8	3.144(3) (2×)
Rb4−O9	3.264(3) (2×)	Rb4−O3	3.403(3) (2×)
$\sum s$[Rb4−O] = 0.75			
In1−O4	2.107(3)	In1−O3	2.109(3)
In1−O8	2.120(3)	In1−O1	2.144(3)
In1−O12	2.187(3)	In1−O13	2.309(3)
$\sum s$[In1−O] = 3.02			
Co1−O6	1.908(3)	Co1−O10	1.927(3)
Co1−O12	1.961(3)	Co1−O13	2.032(3)
$\sum s$[Co(1)−O] = 1.97			
Si1−O1	1.602(3) (2×)	Si1−O2	1.650(3) (2×)
$\sum s$[Si1−O] = 3.99			
Si2−O3	1.596(3)	Si2−O4	1.597(3)
Si2−O2	1.641(3)	Si2−O5	1.657(3)
$\sum s$[Si2−O] = 4.02			
Si3−O8	1.592(3)	Si3−O6	1.601(3)
Si3−O9	1.656(3)	Si3−O7	1.669(3)
$\sum s$[Si3−O] = 3.96			
Si4−O10	1.593(3)	Si4−O12	1.611(3)
Si4−O7	1.632(3)	Si4−O11	1.651(4)
$\sum s$[Si4−O] = 4.03			
Si5−O13	1.598(3)	Si5−O9	1.615(3)
Si5−O5	1.621(3)	Si5−O11	1.632(3)
$\sum s$[Si5−O] = 4.08			

Results and Discussion

Structure. As shown in Figure 1, the structure of **1** is constructed from the following structural elements: five SiO_4

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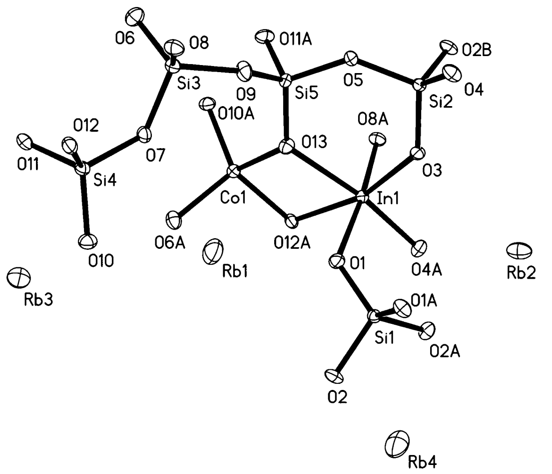

Figure 1. Building units of **1** showing the atom labeling scheme. Thermal ellipsoids are shown at 50% probability.

tetrahedra, one InO_6 octahedron, one CoO_4 tetrahedron, and four Rb sites. The Rb2, Rb4, and Si1 atoms are at 4a special positions with two-fold symmetry, while the other atoms are at general positions. The observed Si−O bond lengths (1.592−1.669 Å, average 1.625 Å) and O−Si−O and $Si-O_{br}-Si$ bond angles (101.1−114.3° for the former and 127.8−147.0° for the latter) are typical values within the normal range. The cobalt ion is divalent, as indicated by bond valence sum. It is tetrahedrally coordinated to four oxygen atoms, two of which are μ_3-O atoms which are bonded to one indium and two silicon atoms. The two polyhedra sharing an edge lead to a significantly distorted InO_6 octahedron, as indicated by the wide range of In−O bond lengths (2.107−2.309 Å) and the small O−In−O bond angle (75.2°) subtended by the CoO_4 tetrahedron. The coordination numbers of the Rb atoms were determined on the basis of the maximum cation−anion distance by Donnay and Allmann.[14] A limit of 3.43 Å was set for Rb−O interactions, which gives the following coordination numbers: Rb1, 9-coordinate; Rb2, 10-coordinate; Rb3 and Rb4, 8-coordinate, with a mean bond length of 3.156, 3.180, 3.034, and 3.197 Å, respectively.

The SiO_4 tetrahedra are connected together by sharing corners to form a new type of silicate single layer in the *ab* plane with the composition $[Si_9O_{26}]^{16-}$ containing rectangular 20-membered rings in a herringbone array (Figure 2a). The composition of a silicate layer is determined by the connectedness *s* of the tetrahedra in the layer and the ratio between different types of Q^s groups.[15] The symbols $Q^s = Q^0$, Q^1, Q^2, Q^3, and Q^4 are used to denote the tetrahedra that share zero to four corners with others. Almost all of the known single layers are composed only of tertiary $[SiO_4]$ tetrahedra with the formula $[Si_{2n}O_{5n}]^{2n-}$. The layer in **1** is composed of secondary and tertiary $[SiO_4]$ tetrahedra in the ratio of 7:2, resulting in a Si:O ratio different from the usual ratio of 2:5. The Si:O ratio of a single layer containing more than one type of $[SiO_4]$ tetrahedra can vary considerably between 2:5.71 (meliphanite) and 2:4.67 ($NaPr[Si_6O_{14}]$).[16,17] The former consists of silicate sheets with square 16-membered rings. To our knowledge, the Si:O ratio for **1**, extending the range to 2:5.78, is the lowest among the known single-layer silicates. The Si:O ratio for **1** is even lower than those for several double-chain silicates, which also consist of secondary and tertiary $[SiO_4]$ tetrahedra.[18] The silicate layers are interconnected by dimers of edge-sharing InO_6 and CoO_4 polyhedra via corner sharing to form a 3D framework with seven- and eight-membered-ring windows within each

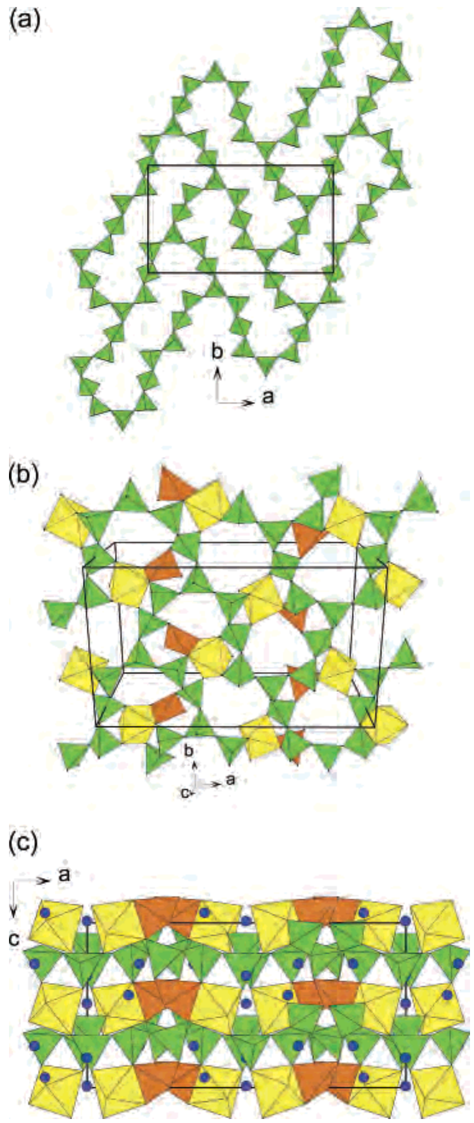

Figure 2. (a) Section of a 20-membered-ring silicate single layer in **1**. (b) Section of the structure showing the connectivity between the silicate single layer and the dimers of edge-sharing InO_6 and CoO_4 polyhedra. (c) Structure of **1** viewed along the *b* axis. The yellow, orange, and green polyhedra represent InO_6 octahedra and CoO_4 and SiO_4 tetrahedra, respectively. Blue circles represent rubidium atoms.

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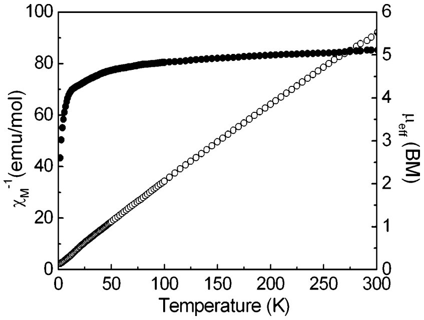

Figure 3. Thermal dependence of μ_{eff} (solid circles) and χ_M^{-1} (open circles) for **1**.

silicate layer (Figure 2b,c). However, adjacent layers are not aligned to form straight channels along the *c* axis. The Rb cations are located within the windows in a silicate layer or at sites between adjacent layers.

Magnetic Susceptibility and SHG. Plots of χ_M^{-1} and μ_{eff} vs T for **1** are shown in Figure 3. The effective magnetic moment at 300 K is 5.1 μ_B, which is in agreement with the observation that the magnetic moments of high-spin tetrahedral and pseudotetrahedral cobalt(II) complexes typically fall within a range between 4.3 and 5.2 μ_B.[19,20] The inverse magnetic susceptibility follows the equation $\chi = C/(T - \theta)$, and a linear fit for $T > 80$ K data gave a Weiss temperature $\theta = -18.7$ K and a Curie constant $C = 3.43$ $cm^3{\cdot}K{\cdot}mol^{-1}$. From the equation $C = N\mu_{eff}/3k_B$, one obtains the effective magnetic moment μ_{eff} per formula unit $= 5.2$ μ_B. The negative Weiss constant together with the decrease in the μ_{eff} values below 80 K is indicative of a dominant antiferromagnetic interaction between the cobalt centers. The absence of a maximum in the χ_M vs T plot indicates the absence of a long-range antiferromagnetic ordering between the spin $S = {}^3/_2$ centers in the solid.

Because compound **1** exhibits high absorption in the spectral range interested in this SHG measurement, for a qualitative work, we collimated and properly focused the laser beam onto the surface of the loaded powder with an incident angle of 45° and collected the SHG signal at its 90° direction. The use of a focused beam is to enhance the SHG efficiency, and the collection of the SHG signal in the backward direction is to minimize the effect of absorption. For a comparison, we also performed the same measurement with the urea powder. The measured peak SHG ($\lambda = 0.532$ μm) intensity of **1** was approximately 20% of that for urea (Figure S2 in the Supporting Information). The nonlinear coefficient of urea is estimated to be 1.4 $pm{\cdot}V^{-1}$.[21] We did not observe any material damage in the experiments under the laser fluence used ($\sim$0.07 $J{\cdot}cm^{-2}$).

In summary, a mixed-metal silicate has been synthesized by a high-temperature, high-pressure hydrothermal method. Its structure is fully characterized by single-crystal X-ray diffraction, SHG, and magnetic susceptibility. The structure consists of 20-membered-ring silicate single layers, which are interconnected by dimers of edge-sharing CoO_4 and InO_6 polyhedra into a 3D framework. It is the first example of transition-metal-incorporated indium silicate. The silicate layer is composed of secondary and tertiary [SiO_4] tetrahedra in the ratio of 7:2, resulting in the lowest Si:O ratio of 2:5.78 among the known single-layer silicates. This work makes an important addition to the structural chemistry of layer silicates. Further research to synthesize new mixed-metal silicates, particularly those containing interesting metal clusters, is in progress.

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Supporting Information Available: Crystallographic data for $Rb_6(InCo)_2(Si_9O_{26})$ in CIF format, experimental and simulated X-ray powder patterns, and SHG measurement results. This material is available free of charge via the Internet at http://pubs.acs.org.

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