Inorganic Chemistry
Article
pubs.acs.org/IC

From an Open Framework to a Layered and a Hexagonal Tungsten Oxide Structure: Controlled Transformation Reactions of an Extended Solid-State Material, $Cs_3Ga_7(SeO_3)_{12}$ to $Ga(OH)(SeO_3)$ and $KGa_3(SeO_4)_2(OH)_6$

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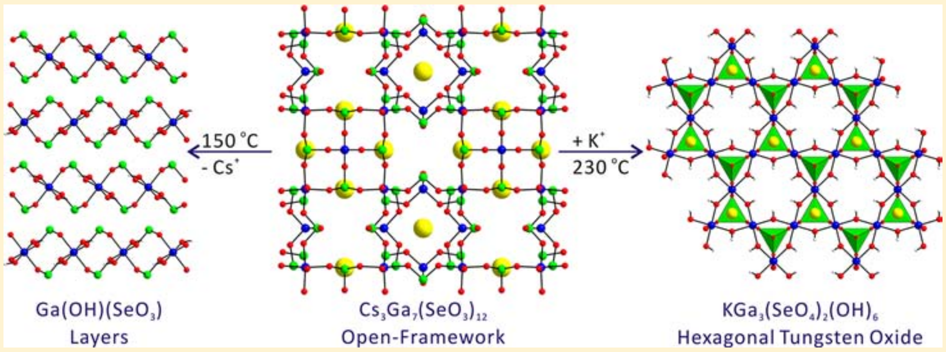
Ⓢ *Supporting Information*



ABSTRACT: A highly symmetric open-framework gallium selenite, $Cs_3Ga_7(SeO_3)_{12}$, containing cubic superlattices has been synthesized by a standard solid-state reaction using Cs_2CO_3, Ga_2O_3, and SeO_2 as reagents. $Cs_3Ga_7(SeO_3)_{12}$ exhibits a three-dimensional open-framework structure consisting of GaO_4 tetrahedra, GaO_6 octahedra, and SeO_3 polyhedra. Step-by-step reactions of the solid-state material in aqueous KNO_3 solution at different temperatures produce $Ga(OH)(SeO_3)$ with a layered structure and $KGa_3(SeO_4)_2(OH)_6$ having a hexagonal tungsten oxide (HTO) topology. Novel HTO layers capped by Se^{6+} cations in $KGa_3(SeO_4)_2(OH)_6$ led us to synthesize other alkali metal gallium selenates, $NaGa_3(SeO_4)_2(OH)_6$ and $RbGa_3(SeO_4)_2(OH)_6$, using hydrothermal reactions. Thermal analyses, infrared spectroscopy, elemental analyses, and dipole moment calculations for the reported materials are also presented.

■ INTRODUCTION

Solid-state materials with extended structural backbones such as chains, layers, and three-dimensional frameworks have been of great interest attributed to their rich structural chemistry. Two representative classes of materials would be the open-framework[1] and the hexagonal tungsten oxide (HTO) materials.[2] While the former has drawn enormous attention owing to their widespread application in catalysis, sorption, ion exchange, and energy storage,[3] the latter has exhibited a variety of excellent applicable characteristics such as optical, piezoelectric, pyroelectric, and adsorption properties.[4] The functional solid-state compounds are generally prepared by standard solid-state or solvothermal reactions at high temperatures and/or under pressures. Therefore, unlike molecular compounds, it is very hard to design and synthesize target materials rationally. Moreover, it is even more difficult to understand detailed mechanisms and kinetics of solid-state reactions. Recently, novel approaches such as time-resolved in situ experiments through the use of diffraction techniques have assisted in helping chemists to elucidate the mechanisms of solid-state reactions;[5] however, there are still many unresolved issues influencing framework formations and subsequent properties of materials. Herein, we report the synthesis and characterization of a novel open-framework quaternary alkali-metal gallium selenite, $Cs_3Ga_7(SeO_3)_{12}$. Although several open-framework selenites have been reported,[6] $Cs_3Ga_7(SeO_3)_{12}$ exhibits unprecedentedly symmetric two kinds of cubic superlattices. We also demonstrate how the open-framework structure transforms to a layered and a hexagonal tungsten oxide (HTO) material under mild hydrothermal conditions. With isostructural HTO materials, the magnitude of distortions for the SeO_4 tetrahedra is analyzed by local dipole moment calculations and an explanation is given by the effect of alkali-metal cation size.

■ EXPERIMENTAL SECTION

Reagents. Na_2CO_3 (Hayashi, 99.5%), K_2CO_3 (Jin, 99.5%), Cs_2CO_3 (Aldrich, 99.0%), Ga_2O_3 (Alfa Aesar, 99.999%), $Ga(NO_3)_3 \cdot xH_2O$ (Alfa Aesar, 99.9%), SeO_2 (Aldrich, 98%), and H_2SeO_4 (Aldrich, 99.95%) were used as received.

Received: July 29, 2013
Published: October 21, 2013

dx.doi.org/10.1021/ic402274s | *Inorg. Chem.* 2013, 52, 12726−12730

Table 1. Crystallographic Data for $Cs_3Ga_7(SeO_3)_{12}$, $NaGa_3(SeO_4)_2(OH)_6$, $KGa_3(SeO_4)_2(OH)_6$, and $RbGa_3(SeO_4)_2(OH)_6$

formula	$Cs_3Ga_7Se_{12}O_{36}$	$NaGa_3Se_2O_{14}H_6$	$KGa_3Se_2O_{14}H_6$	$RbGa_3Se_2O_{14}H_6$
fw	2410.29	620.12	636.23	682.60
space group	*Pm*-3*n* (No. 223)	*R*-3*m* (No. 166)	*R*-3*m* (No. 166)	*R*-3*m* (No. 166)
a (Å)	12.7106(10)	7.2325(10)	7.2476(10)	7.2641(10)
b (Å)	12.7106(10)	7.2325(10)	7.2476(10)	7.2641(10)
c (Å)	12.7106(10)	17.262(2)	17.746(2)	18.141(3)
V (Å^3)	2053.52(3)	782.0(3)	807.25(3)	829.0(3)
Z	2	3	3	3
T (°K)	298.0(2)	298.0(2)	298.0(2)	298.0(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
ρ_{calcd} (g cm^{-3})	3.898	3.950	3.926	4.102
μ (mm^{-1})	17.884	14.806	14.689	18.304
$R(F)^a$	0.0161	0.0150	0.0223	0.0182
$R_w(F_o^2)^b$	0.0301	0.0320	0.0590	0.0511

$^aR(F) = \Sigma \,||F_o| - |F_c||/\Sigma\, |F_o|$. $^bR_w(F_o^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table 2. Selected Bond Distances (Angstroms) for $Cs_3Ga_7(SeO_3)_{12}$, $NaGa_3(SeO_4)_2(OH)_6$, $KGa_3(SeO_4)_2(OH)_6$, and $RbGa_3(SeO_4)_2(OH)_6$

$Cs_3Ga_7(SeO_3)_{12}$		$NaGa_3(SeO_4)_2(OH)_6$		$KGa_3(SeO_4)_2(OH)_6$		$RbGa_3(SeO_4)_2(OH)_6$	
Se(1)−O(1)	1.705(3)	Se(1)−O(1) × 3	1.645(2)	Se(1)−O(1) × 3	1.647(3)	Se(1)−O(1) × 3	1.646(3)
Se(1)−O(2) × 2	1.6685(17)	Se(1)−O(3)	1.619(3)	Se(1)−O(3)	1.619(6)	Se(1)−O(3)	1.621(5)
Ga(1)−O(1) × 4	1.832(2)	Ga(1)−O(1) × 2	2.0355(19)	Ga(1)−O(1) × 2	2.030(3)	Ga(1)−O(1) × 2	2.023(3)
Ga(2)−O(2) × 6	1.9526(16)	Ga(1)−O(2) × 4	1.9364(17)	Ga(1)−O(2) × 4	1.9422(10)	Ga(1)−O(2) × 4	1.9475(10)
Cs(1)−O(2) × 8	3.2752(18)	Na(1)−O(1) × 6	2.781(2)	K(1)−O(1) × 6	2.825(3)	Rb(1)−O(1) × 6	2.864(3)
Cs(1′)−O(1) × 3	3.605(11)	Na(1)−O(2) × 6	2.870(2)	K(1)−O(2) × 6	2.958(3)	Rb(1)−O(2) × 6	3.025(3)
Cs(1′)−O(2) × 4	3.295(2)						
Cs(1′)−O(2) × 4	3.320(3)						

Syntheses. Crystals of $Cs_3Ga_7(SeO_3)_{12}$ were grown by a standard solid-state reaction. Under an atmosphere of dry argon, 0.325 g (1.00×10^{-3} mol) of Cs_2CO_3, 0.187 g (1.00×10^{-3} mol) of Ga_2O_3, and 0.665 g (6.00×10^{-3} mol) of SeO_2 were thoroughly mixed with an agate mortar and pestle. The reaction mixture was introduced into a fused silica tube that was subsequently evacuated and sealed. The tube was gradually heated to 350 °C for 5 h and 500 °C for 48 h and cooled at a rate of 6 °C h^{-1} to room temperature. The product contained colorless block-shaped crystals of $Cs_3Ga_7(SeO_3)_{12}$ and some unknown amorphous phases. Pure polycrystalline $Cs_3Ga_7(SeO_3)_{12}$ was synthesized through a similar reaction by combining a stoichiometric amount of starting reagents heated at 400 °C for 24 h with an intermediate regrinding. In addition, we will discuss more in detail later; after obtaining crystals of $KGa_3(SeO_4)_2(OH)_6$ from a transformation reaction of $Cs_3Ga_7(SeO_3)_{12}$, a complete series of $AGa_3(SeO_4)_2(OH)_6$ (A = Na, K, and Rb) crystals was prepared by hydrothermal reactions. For $NaGa_3(SeO_4)_2(OH)_6$, 0.106 g (1.00×10^{-3} mol) of Na_2CO_3, 0.187 g (1.00×10^{-3} mol) of Ga_2O_3, 0.5 mL of H_2SeO_4, and 2 mL of water were combined. With $AGa_3(SeO_4)_2(OH)_6$ (A = K and Rb), 1.00×10^{-3} mol of A_2CO_3, 0.511 g (2.00×10^{-3} mol) of $Ga(NO_3)_3 \cdot xH_2O$, 0.222 g (2.00×10^{-3} mol) of SeO_2, and 1 mL of water were combined. The respective reaction mixtures were placed in 23 mL Teflon-lined stainless steel autoclaves. The autoclaves were sealed and heated to 230 °C to generate autogenous pressures, held for 4 days, and cooled to room temperature at a rate of 6 °C h^{-1}. After cooling, the autoclaves were opened and the products were recovered by filtration and washed with distilled water. Colorless trigonal prismatic crystals of $NaGa_3(SeO_4)_2(OH)_6$, $KGa_3(SeO_4)_2(OH)_6$, and $RbGa_3(SeO_4)_2(OH)_6$ were obtained in 48%, 42%, and 35% yields, respectively, based on the corresponding alkali metal carbonates. Powder X-ray diffraction patterns on the synthesized products show the materials are single phases and are in good agreement with the generated patterns from the single-crystal data (see the Supporting Information).

Single-Crystal X-ray Diffraction. Structures of the reported materials were determined by a standard crystallographic method. A colorless block crystal for $Cs_3Ga_7(SeO_3)_{12}$ and colorless trigonal prismatic crystals for $AGa_3(SeO_4)_2(OH)_6$ were used for single-crystal data analyses. All of the data were collected using a Bruker SMART BREEZE diffractometer equipped with a 1K CCD area detector using graphite-monochromated Mo Kα radiation at room temperature. A hemisphere of data was collected using a narrow-frame method with scan widths of 0.30° in omega and an exposure time of 10 s/frame. The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability. The maximum correction applied to the intensities was <1%. Data were integrated using the SAINT program,[7] with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption attributable to the variation in the path length through the detector faceplate. A semiempirical absorption correction was made on the hemisphere of data with the SADABS program.[8] Data were solved and refined using SHELXS-97[9] and SHELXL-97,[10] respectively. All calculations were performed using the WinGX-98 crystallographic software package.[11] Crystallographic data and selected bond distances for the reported materials are given in Tables 1 and 2.

Powder X-ray Diffraction. Powder X-ray diffraction was used to confirm the phase purity of the synthesized materials. Powder XRD patterns were collected on a Bruker D8-Advance diffractometer using Cu Kα radiation at room temperature with 40 kV and 40 mA. Polycrystalline samples were mounted on sample holders and scanned in the 2θ range 5−70° with a step size of 0.02° and step time of 1 s.

Infrared Spectroscopy. Infrared spectra were recorded on a Varian 1000 FT-IR spectrometer in the 400−4000 cm^{-1} range, with the sample embedded in a KBr matrix.

Thermogravimetric Analysis. Thermogravimetric analyses were performed on a Setaram LABSYS TG-DTA/DSC Thermogravimetric Analyzer. Polycrystalline samples were contained within alumina crucibles and heated at a rate of 10 °C min^{-1} from room temperature to 1000 °C under flowing argon.

Scanning Electron Microscope/Energy-Dispersive Analysis by X-ray (SEM/EDAX). SEM/EDAX analysis was performed using a Hitachi S-3400N/Horiba Energy EX-250 instruments. EDAX for $Cs_3Ga_7(SeO_3)_{12}$, $NaGa_3(SeO_4)_2(OH)_6$, $KGa_3(SeO_4)_2(OH)_6$, and

$RbGa_3(SeO_4)_2(OH)_6$ reveal A:Ga:Se ratios of approximately 3.2:7.0:11.5, 1.0:3.0:1.6, 1.0:3.1:2.0, and 1.1:3.0:2.0, respectively.

Transformation Reactions. Transformation reactions were performed by stirring ca. 100 mg of polycrystalline $Cs_3Ga_7(SeO_3)_{12}$ in 5 mL of 1 M HCl (aq) and 1 M KNO_3 (aq) solutions. Reactions were performed at room temperature, 100, 150, and 230 °C for 24 h. Reaction products were recovered by filtration, washed with excess water, and dried in air for 1 day.

■ RESULTS AND DISCUSSION

Structure of $Cs_3Ga_7(SeO_3)_{12}$. $Cs_3Ga_7(SeO_3)_{12}$ has a three-dimensional open-framework structure consisting of GaO_4 tetrahedra, GaO_6 octahedra, and SeO_3 polyhedra that are connected through oxygen atoms (see Figure 1). Within an asymmetric unit, two unique Ga^{3+} cations exist. Each $Ga(1)^{3+}$ is bonded to four oxygen atoms in a tetrahedral coordination environment with four identical $Ga(1)^{3+}-O$ bond distances of 1.832(2) Å, whereas $Ga(2)^{3+}$ is linked to six oxygen atoms in an octahedral geometry in which the observed unique length for the $Ga(2)^{3+}-O$ bond is 1.9526(16) Å. Se^{4+} cations are in an asymmetric distorted trigonal pyramidal coordination environment attributed to their lone pairs. $Se^{4+}-O$ bond lengths range from 1.6685(17) to 1.705(3) Å. Cs^+ cations are disordered over two different positions, Cs(1) and Cs(1′), with refined fractional occupancies of 0.31(4) and 0.35(2), respectively.

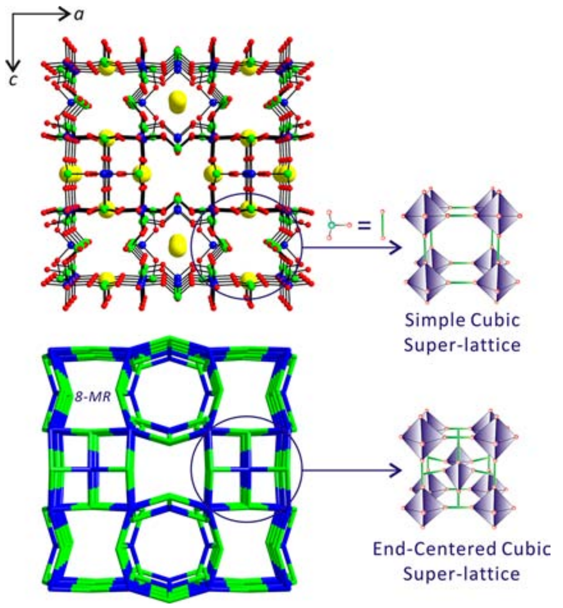


Figure 1. Ball-and-stick and wire diagrams of $Cs_3Ga_7(SeO_3)_{12}$ in the *ac* plane (blue, Ga; green, Se; yellow, Cs; red, O). Note the structural backbone is a three-dimensional open framework composed of simple and end-centered cubic superlattices.

The structural backbone of $Cs_3Ga_7(SeO_3)_{12}$ may be considered as a three-dimensional open framework composed of three, mutually perpendicular, eight-membered rings (8-MR) running parallel to the [100], [010], and [001] directions. An approximate dimension of the channel is 2.5 × 4.8 Å, as defined by the shortest oxygen−oxygen contact taking into account the atomic radii from Shannon.[12] Interestingly, highly symmetric cubic building blocks are observed from the framework of $Cs_3Ga_7(SeO_3)_{12}$. Linkages between GaO_6 octahedra and SeO_3 linkers result in simple cubic superlattices (see Figure 1). In addition, each parallel side of the cubic superlattices is occupied by GaO_4 tetrahedra, which generates other superlattices, i.e., end-centered cubic building blocks (see Figure 1). In connectivity terms, the structure of $Cs_3Ga_7(SeO_3)_{12}$ can be formulated as an anionic framework of $\{4[GaO_{6/2}]^{3-}3\text{-}[GaO_{4/2}]^{-}12[SeO_{3/2}]^{+}\}^{3-}$. Charge neutrality is retained by the three Cs^+ cations residing in the channels. Bond valence sum calculations on $Cs_3Ga_7(SeO_3)_{12}$ reveal values of 0.87, 4.11, 3.01−3.21, and 2.04−2.06 for Cs^+, Se^{4+}, Ga^{3+}, and O^{2-}, respectively.[13] A moderate open-framework structure of $Cs_3Ga_7(SeO_3)_{12}$ led us to calculate the amount of void space after removing the nonframework species, Cs^+ cations. For $Cs_3Ga_7(SeO_3)_{12}$, the amount of void space is calculated to be 16.9% using the CALC SOLV command in PLATON.[14] If the Cs^+ cations are included in the calculation, however, the void space for $Cs_3Ga_7(SeO_3)_{12}$ becomes 4.4%. The stereoactive lone pairs on Se^{4+} cations are pointing toward the center of channels, which may occupy the void space as well.

Transformation Reactions. The open-framework nature of $Cs_3Ga_7(SeO_3)_{12}$ suggested the possibility of ion-exchange reactions in which the Cs^+ cations could be replaced by other cations. Thus, several ion-exchange attempts have been made on polycrystalline $Cs_3Ga_7(SeO_3)_{12}$ in 1 M aqueous solutions of

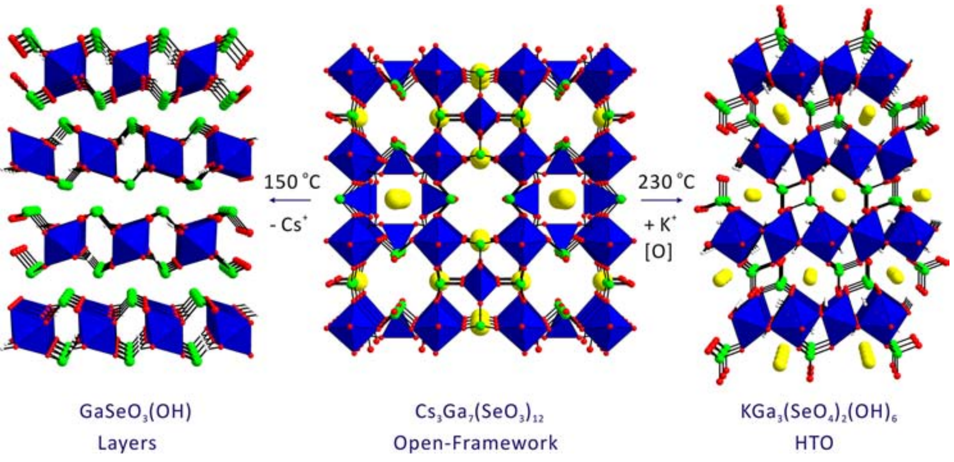


Figure 2. Schematic structural representations for the transformation of $Cs_3Ga_7(SeO_3)_{12}$ to $GaSeO_3(OH)$ at 150 °C and to $KGa_3(SeO_4)_2(OH)_6$ at 230 °C in aqueous KNO_3 solution (blue, Ga; green, Se; yellow, Cs or K; red, O; white, H). Note how the open-framework structure changes to a layered and a HTO structure.

KNO_3 from room temperature to 100 °C. Unfortunately, we were not able to replace the Cs^+ cation for K^+, which might be attributable to the smaller size of the channel windows. However, once the reaction temperature was elevated to 150 °C, a layered material, $Ga(OH)(SeO_3)$,[6e] was obtained in 31% yield with a very small amount of $Ga_2(SeO_3)_3(H_2O)_3$[15] on the basis of powder XRD pattern (see Figure 2). The layered geometry may be obtained from the rupture of the framework wall existing in the cubic superlattices when the huge Cs^+ cations locked in place started escaping from the channel at 150 °C. In addition, if $Cs_3Ga_7(SeO_3)_{12}$ is instead heated to 230 °C, an oxidation reaction occurred and novel trigonal prismatic crystals of $KGa_3(SeO_4)_2(OH)_6$ with a hexagonal tungsten oxide (HTO) structure were exclusively obtained in 45% yield, which was confirmed by X-ray single-crystal diffraction analysis (see Figure 2). On the basis of the reaction condition we used, the reactants seem to transform through a dissolution−reprecipitation process rather than to occur through a topotactic reaction.

Structures of $AGa_3(SeO_4)_2(OH)_6$ (A = Na, K, and Rb). After obtaining crystals of $KGa_3(SeO_4)_2(OH)_6$ from the transformation reaction of $Cs_3Ga_7(SeO_3)_{12}$ in 1 M aqueous solutions of KNO_3 at 230 °C we were able to successfully synthesize crystals of $NaGa_3(SeO_4)_2(OH)_6$ and $RbGa_3(SeO_4)_2(OH)_6$ through hydrothermal reactions (see Experimental Section). All three reported alkali-metal gallium selenates, $AGa_3(SeO_4)_2(OH)_6$ (A = Na, K, and Rb), are isostructural and crystallize in rhombohedral space group *R*-3*m* (No. 166) (see Table 1). Thus, only a brief structural explanation of $KGa_3(SeO_4)_2(OH)_6$ will be given here. As seen in Figure 3, $KGa_3(SeO_4)_2(OH)_6$ exhibits a layered HTO structure composed of corner-shared $GaO_2(OH)_4$ octahedra, which results in three- and six-membered rings. Ga−O bond distances lie in the range 1.9422(10)−2.030(3) Å. SeO_4 tetrahedra serve as intralayer linkers by capping the $GaO_2(OH)_4$ octahedra from above and below. Se−O bond lengths range from 1.619(6) to 1.647(3) Å. Although there is an example of HTO containing S^{6+} cations[16] that can be replaced by Se^{6+}, $KGa_3(SeO_4)_2(OH)_6$ is a novel layered HTO material capped by solely Se^{6+} cations. We observe that hydrogen bonds occur from the terminal oxygen atom, O(3), in the SeO_4 tetrahedra to the corner-shared oxygen atom, O(2), in the $GaO_2(OH)_4$ octahedra [O(2)···O(3) 2.918(3) Å]. The K^+ cation is in a 12-fold coordination environment with K−O contacts ranging from 2.825(3) to 2.958(3) Å. In connectivity terms, the structure can be described as an anionic layer of $\{3[GaO_{2/2}(OH)_{4/2}]^{-1}2[SeO_{3/2}O_{1/1}]^{+1}\}^{-1}$. Charge neutrality is maintained by the K^+ cation residing in between the anionic layers.

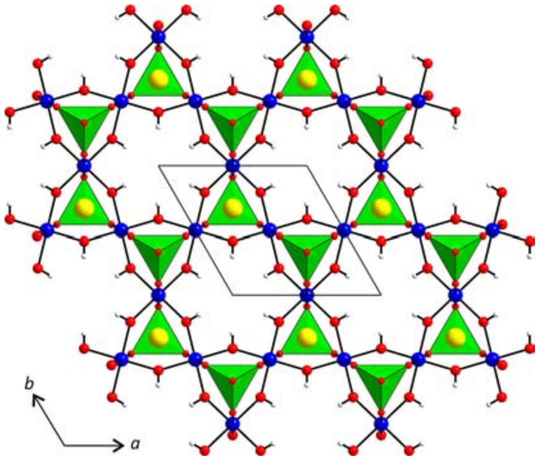


Figure 3. Ball-and-stick and polyhedral representation of one layer of $AGa_3(SeO_4)_2(OH)_6$ in the *ab* plane (green, Se; blue, Ga; yellow, Na, K, or Rb; red, O).

Thermogravimetric Analyses (TGA). Thermal analyses reveal that all of the reported materials are stable up to about 400 °C. Above the temperature, the materials decompose attributable to loss of SeO_2 and/or H_2O. Powder XRD patterns on the calcined products show that $Cs_3Ga_7(SeO_3)_{12}$ and $NaGa_3(SeO_4)_2(OH)_6$ decompose to Ga_2O_3 and some unknown amorphous phases. $KGa_3(SeO_4)_2(OH)_6$ and $RbGa_3(SeO_4)_2(OH)_6$ break down to mixtures of $KGa_{11}O_{17}$ (PDF-#32-0788) and Ga_2O_3 (PDF-#41-1103) and $RbGa_{11}O_{17}$ (PDF-#26-0933) and Ga_2O_3, respectively. Thermogravimetric analysi diagrams have been deposited to the Supporting Information.

Infrared Spectroscopy. Infrared spectra of the materials show the Ga−O and Se−O vibrations at around 532−571 and 742−876 cm^{-1}, respectively. With $AGa_3(SeO_4)_2(OH)_6$, absorptions arising from the −OH and those for the hydrogen bonds are observed from 3415 to 3639 and 2158 to 2259 cm^{-1}, respectively. Assignments are consistent with those previously reported.[17]

Dipole Moment Calculations. The magnitude of the distortions for the SeO_3 trigonal pyramid and SeO_4 tetrahedra in the reported materials can be quantified by determining the local dipole moments using bond valence sum calculations.[18] Using this methodology, the local dipole moment for the unique SeO_3 polyhedron in $Cs_3Ga_7(SeO_3)_{12}$ is calculated to be about 7.61 D (D = Debyes), which is consistent with those reported dipole moments for the SeO_3 polyhedra.[19] Also, using similar calculations, local dipole moments for SeO_4 tetrahedra in $NaGa_3(SeO_4)_2(OH)_6$, $KGa_3(SeO_4)_2(OH)_6$, and $RbGa_3(SeO_4)_2(OH)_6$ are determined to be 0.08, 0.47, and 0.85 D, respectively. Although the values of dipole moments are not very large attributable to the tetrahedral geometry, one can notice that the magnitude of distortions for SeO_4 terahedra increases as the size of alkali-metal cations increases. Since all three materials are isostructural, the alkali-metal cations reside between the $GaO_2(OH)_4$ layers with the same AO_{12} coordination environments. Taken from Shannon,[12] the average radii for 12-coordinate Na^+, K^+, and Rb^+ are 1.39, 1.64, and 1.72 Å, respectively. The increasing size of the alkali metal forces the $GaO_2(OH)_4$ layers further apart. At the same time, there are strong hydrogen bonds between the terminal oxygen atom, O(3), in the SeO_4 tetrahedra and the corner-shared oxygen atom, O(2), in the $GaO_2(OH)_4$ octahedra. Thus, to maintain the HTO structures, the SeO_4 tetrahedra should distort more as the size of alkali metals increases (see Figure 4).

■ CONCLUSIONS

We synthesized a new quaternary cesium gallium selenite, $Cs_3Ga_7(SeO_3)_{12}$, with an open-framework structure composed of two kinds of cubic superlattices. Reactions of $Cs_3Ga_7(SeO_3)_{12}$ with aqueous KNO_3 under hydrothermal conditions at 150 and 230 °C result in a layered gallium selenite, $Ga(OH)(SeO_3)$, and an alkali-metal gallium selenate, $KGa_3(SeO_4)_2(OH)_6$, with a hexagonal tungsten oxide (HTO) structure, respectively. We successfully demonstrated that a

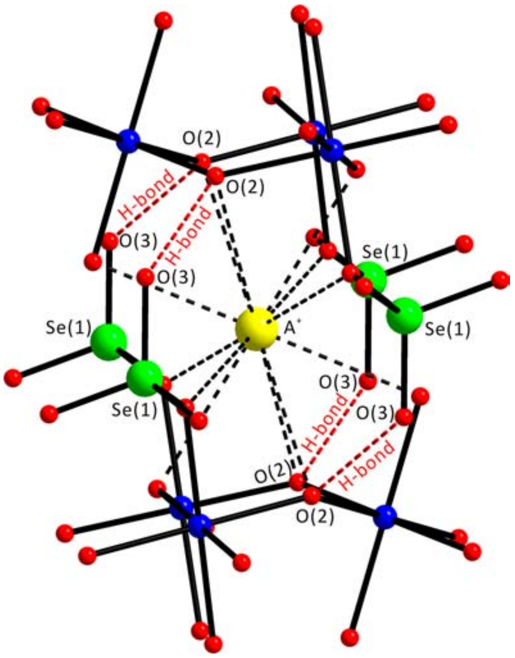


Figure 4. Ball-and-stick model of $AGa_3(SeO_4)_2(OH)_6$ showing how the size of alkali-metal cations influences the hydrogen bonds and the distortion of SeO_4 tetrahedra (green, Se; blue, Ga; yellow, Na, K, or Rb; red, O).

solid-state compound with an extended structure can be transformed to novel materials under mild conditions in a controlled manner. After obtaining crystals of $KGa_3(SeO_4)_2(OH)_6$ from a transformation reaction of $Cs_3Ga_7(SeO_3)_{12}$, phase pure crystals of $NaGa_3(SeO_4)_2(OH)_6$ and $RbGa_3(SeO_4)_2(OH)_6$ were also successfully synthesized and fully characterized.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data in CIF format, experimental and calculated powder XRD patterns, thermogravimetric analysis diagrams, and infrared spectra for $Cs_3Ga_7(SeO_3)_{12}$ and $AGa_3(SeO_4)_2(OH)_6$ (A = Na, K, and Rb). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science & Technology (grant 2013R1A2A2A01007170).

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