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A Series of New Ternary and Quaternary Compounds in the $Li^{I}-Ga^{III}-Te^{IV}-O$ System

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Systematic explorations of new compounds in the $Li^{I}-Ga^{III}-Te^{IV}-O$ system led to two new isomeric ternary gallium tellurites, namely, α-$Ga_2(TeO_3)_3$ and β-$Ga_2(TeO_3)_3$, and two new quaternary lithium gallium tellurites, namely, $HLi_2Ga_3(TeO_3)_6(H_2O)_6$ and $Li_9Ga_{13}Te_{21}O_{66}$. α-$Ga_2(TeO_3)_3$ is a noncentrosymmetric structure ($I\bar{4}3d$) and displays a moderately strong second-harmonic-generation response that is comparable with that of KDP (KH_2PO_4). Its structure features a condensed three-dimensional (3D) network alternatively connected by GaO_4 tetrahedra and TeO_3 trigonal pyramids via corner sharing. β-$Ga_2(TeO_3)_3$ is centrosymmetric ($P6_3/m$) and features a 3D open framework composed of Ga_2O_9 dimers bridged by TeO_3 groups with one-dimensional (1D) 12-MR channels along the *c* axis. Although both $HLi_2Ga_3(TeO_3)_6(H_2O)_6$ and $Li_9Ga_{13}Te_{21}O_{66}$ crystallized in the same space group $R\bar{3}$, they belong to different structure types. The structure of $HLi_2Ga_3(TeO_3)_6(H_2O)_6$ can be viewed as the 1D tunnels of the 3D gallium tellurite being occupied by Li^+ and H^+ ions whereas the structure of $Li_9Ga_{13}Te_{21}O_{66}$ is a complicated 3D framework composed of alternating gallium tellurite layers and GaO_6 octahedral layers with Li^+ cations being located at the cavities of the structure. Optical diffuse-reflectance spectrum measurements indicate that all four compounds are insulators and transparent in the range of 300−2500 nm.

Introduction

The search for a new second-order nonlinear optical (NLO) material is of current interest and great importance because of their applications in photonic technologies.[1] Metal selenites and tellurites can adopt many unusual structures because of the presence of stereochemically active lone pairs that can serve as structure-directing agents.[2] It is reported that the combination of transition-metal ions with d^0 electronic configuration, such as W^{6+} and Mo^{6+}, and lone pairs containing Se^{IV} and Te^{IV} cations, both susceptible to second-order Jahn−Teller distortions, can form inorganic solids with excellent second-harmonic-generation (SHG) properties.[3−5] Recently, we found that the combination of a BO_4 tetrahedron and a lone pair containing a Se^{IV} cation can also afford a new type of second-order NLO compound, $Se_2B_2O_7$.[6] So far, no $B^{III}-Te^{IV}-O$ compounds have been reported, and reports on ternary or quaternary $Ga^{III}-Te^{IV}-O$ phases are rather scarce. To our best knowledge, only two compounds, namely, $Ga_2Te_4O_{11}$ ($P1$) and $Ga_2(TeO_3)_3(H_2O)_3$ ($R3c$), have been structurally characterized in the ternary $Ga^{III}-Te^{IV}-O$ family.[7] Both compounds are crystallized in noncentrosymmetric space groups. As for the quaternary $Ga^{III}-Te^{IV}-O$ phases, two sodium gallium tellurites [$NaGaTe_2O_6$ and $Na(GaTe_2O_6)\cdot 2.4H_2O$], two potassium gallium tellurites [$K(GaTe_6O_{14})$ and $K(GaTe_2O_6)\cdot 1.8H_2O$], and one molybdenum gallium tellurite ($Ga_2MoTe_2O_{10}$) have been reported.[8] They exhibit five different types of structures. So far, no compounds in the $Li^{I}-Ga^{III}-Te^{IV}-O$ system has been reported. The smaller ionic radius of Li^{I} compared with other alkali-metal ions may lead to new compounds with different structures and unique physical properties. Our systematic explorations in the $Li^{I}-Ga^{III}-Te^{IV}-O$ system resulted in two new isomeric gallium(III) tellurites [α-$Ga_2(TeO_3)_3$ and

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(1) Chen, C.; Liu, G. *Annu. Rev. Mater. Sci.* **1986**, *16*, 203.

(2) (a) Wickleder, M. S. *Chem. Rev.* **2002**, *102*, 2011 and references cited therein. (b) Verma, V. P. *Thermochim. Acta* **1999**, *327*, 63 and references cited therein. (c) Ok, K. M.; Halasyamani, P. S. *Chem. Soc. Rev.* **2006**, *35*, 710.

(3) (a) Ra, H.-S.; Ok, K.-M.; Halasyamani, P. S. *J. Am. Chem. Soc.* **2003**, *125*, 7764. (b) Ok, K.-M.; Halasyamani, P. S. *Inorg. Chem.* **2004**, *43*, 4248.

(4) (a) Hart, R. T.; Ok, K.-M.; Halasyamani, P. S.; Zwanziger, J. W. *Appl. Phys. Lett.* **2004**, *85*, 938. (b) Goodey, J.; Broussard, J.; Halasyamani, P. S. *Chem. Mater.* **2002**, *14*, 3174.

(5) (a) Johnston, M. G.; Harrison, W. T. A. *Inorg. Chem.* **2001**, *40*, 6518. (b) Balraj, V.; Vidyasagar, K. *Inorg. Chem.* **1999**, *38*, 5809.

(6) (a) Kong, F.; Huang, S.-P.; Sun, Z.-M.; Mao, J.-G.; Cheng, W.-D. *J. Am. Chem. Soc.* **2006**, *128*, 7750. (b) Mao, J.-G.; Jiang, H.-L.; Kong, F. *Inorg. Chem.* **2008**, *47*, 8498.

(7) (a) Dutreilh, M.; Thomas, P.; Champarnaud-Mesjard, J.-C.; Frit, B. *Solid State Sci.* **2001**, *3*, 423. (b) Weil, M.; Stoeger, B. *Acta Crystallogr., Sect. E* **2007**, *63*, i202.

(8) (a) Miletich, R.; Pertlik, F. *J. Alloys Compd.* **1998**, *268*, 107. (b) Bhuvanesh, N. S. P.; Halasyamani, P.-S. *Inorg. Chem.* **2001**, *40*, 1404. (c) Ok, K.-M.; Halasyamani, P.-S. *Chem. Mater.* **2001**, *13*, 4278. (d) Kong, F.; Hu, C.-L.; Hu, T.; Zhou, Y.; Mao, J.-G. *Dalton Trans.* **2009**, 4962.

β-$Ga_2(TeO_3)_3$] and two new lithium(I) gallium(III) tellurites [$HLi_2Ga_3(TeO_3)_6(H_2O)_6$ and $Li_9Ga_{13}Te_{21}O_{66}$]. They belong to four types of structures. More interestingly, the acentric α-$Ga_2(TeO_3)_3$ ($I\bar{4}3d$) displays a SHG response comparable to that of KDP (KH_2PO_4). Herein we report their syntheses, crystal structures, and physical properties.

Experiment Section

Materials and Instrumentation. All of the chemicals were analytically pure from commercial sources and used without further purification. TeO_2 was purchased from Acros Organics (99%+). Li_2CO_3 and Ga_2O_3 were obtained from Sinopharm Chemical Reagent Co., Ltd. (98%+). $Ga(NO_3)_3$ was purchased from Alfa Aesar China (Tianjin) Co. Ltd. (99.9%). Powder X-ray diffraction (XRD) patterns were collected on a XPERT-MPD $\theta-2\theta$ diffractometer using graphite-monochromated Cu Kα radiation in the angular range $2\theta = 5-85°$ with a step size of 0.05°. IR spectra were recorded on a Magna 750 FT-IR spectrometer as KBr pellets in the range of 4000−400 cm^{-1}. Optical diffuse-reflectance and absorption spectra were measured at room temperature with a PE Lambda 900 UV−visible spectrophotometer. A $BaSO_4$ plate was used as the standard (100% reflectance). The absorption spectrum was calculated from reflectance spectra using the Kubelka−Munk function: $\alpha/S = (1 - R)^2/2R$,[10] where α is the absorption coefficient, *S* is the scattering coefficient, which is practically wavelength-independent when the particle size is larger than 5 μm, and *R* is the reflectance. Thermogravimetric analysis (TGA) was carried out with a Netzsch STA 449C unit at a heating rate of 5 °C/min under a static air atmosphere. Differential thermal analysis (DTA) was performed under N_2 on a Netzsch DTA404PC. The sample and reference (Al_2O_3) were enclosed in platinum crucibles, heated from room temperature to 780 °C, and then cooled to room temperature at a rate of 5 °C/min. Thermogravimetric−mass spectrometric (TG−MS) analysis was carried out on preweighted samples in a nitrogen stream using a Netzsch STA449C-QMS403C apparatus. The measurements of the powder frequency-doubling effect were carried out on a sieved (80−100 mesh) powder sample of α-$Ga_2(TeO_3)_3$ by means of the modified method of Kurtz and Perry.[11] The fundamental wavelength was 1064 nm, generated by a Q-switched Nd:YAG laser. The SHG wavelength was 532 nm. KDP sieved powder (80−100 mesh) was used as the reference to assume the effect.

Preparations of α-$Ga_2(TeO_3)_3$, β-$Ga_2(TeO_3)_3$, $HLi_2Ga_3(TeO_3)_6(H_2O)_6$, and $Li_9Ga_{13}Te_{21}O_{66}$. The four compounds were hydrothermally synthesized by reactions of a mixture of Ga_2O_3 (or $Ga(NO_3)_3$), TeO_2, and Li_2CO_3 in 3−6 mL of distilled water at 200 or 230 °C for 7 days. The loaded compositions are as follows: Ga_2O_3 (0.0375 g, 0.20 mmol), TeO_2 (0.0958 g, 0.60 mmol), Li_2CO_3 (0.0074 g, 0.10 mmol), and H_2O (6 mL) for α-$Ga_2(TeO_3)_3$; Ga_2O_3 (0.0375 g, 0.20 mmol), TeO_2 (0.0958 g, 0.60 mmol), Li_2CO_3 (0.0185 g, 0.25 mmol), and H_2O (6 mL) for β-$Ga_2(TeO_3)_3$; $Ga(NO_3)_3$ (0.0307 g, 0.12 mmol), TeO_2 (0.0383 g, 0.24 mmol), Li_2CO_3 (0.0259 g, 0.35 mmol), and H_2O (3 mL) for $HLi_2Ga_3(TeO_3)_6(H_2O)_6$; Ga_2O_3 (0.0375 g, 0.2 mmol), TeO_2 (0.0958 g, 0.6 mmol), Li_2CO_3 (0.0259 g, 0.35 mmol), and H_2O (6 mL) for $Li_9Ga_{13}Te_{21}O_{66}$. The mixtures were sealed into an autoclave equipped with a Teflon liner (23 mL) and heated at 200 °C for $HLi_2Ga_3(TeO_3)_6(H_2O)_6$ and 230 °C for the other three compounds for 7 days. Colorless tetrahedral-shaped crystals of α-$Ga_2(TeO_3)_3$ were collected in ca. 60% yield (based on Te). Needle-shaped β-$Ga_2(TeO_3)_3$ crystals were collected in a very low yield (< 10.0 mg); the impurities are unknown white powders. A lot of effort was invested in trying to optimize the yield for β-$Ga_2(TeO_3)_3$ by mild hydrothermal syntheses and solid-state reactions but was unsuccessful. Furthermore, if Li_2CO_3 was not added or being replaced by other metal carbonates and NH_4OH, both α-$Ga_2(TeO_3)_3$ and β-$Ga_2(TeO_3)_3$ cannot be isolated. Rhombic $HLi_2Ga_3(TeO_3)_6(H_2O)_6$ and hexagonal $Li_9Ga_{13}Te_{21}O_{66}$ crystals were collected in ca. 20% and 30% yield (based on Te), respectively. The microcrystalline impurities in the products were filtered off. IR data (KBr, cm^{-1}) for α-$Ga_2(TeO_3)_3$: 814 m, 748 s, 690 s, 440 s. IR data (KBr, cm^{-1}) for β-$Ga_2(TeO_3)_3$: 688 br s, 503 s. IR data (KBr, cm^{-1}) for $HLi_2Ga_3(TeO_3)_6(H_2O)_6$): 860 m, 683 s, 495 s. IR data (KBr, cm^{-1}) for $Li_9Ga_{13}Te_{21}O_{66}$: 749 m, 694 s, 545 m. Powder XRD patterns on the four compounds are in agreement with the generated patterns from their single-crystal data, indicating that all samples are pure and can be used for other physical property measurements (see the Supporting Information).

Crystal Structure Determination. Data collection for the four compounds was performed on a Rigaku Mercury Saturn 70 CCD diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) at 293 K. The data sets were corrected for Lorentz and polarization factors as well as for absorption by a multiscan method.[9a] The structures were solved by direct methods and refined by full-matrix least-squares fitting on F^2 by *SHELX-97*.[9b] All non-H atoms were refined with anisotropic thermal parameters. For α-$Ga_2(TeO_3)_3$, Ga1 at a $\bar{4}$ site is not fully occupied and its site occupancy factor was fixed at 0.2222 for the sake of charge balance. For the same reason, the site occupancy factor of Ga2 in $Li_9Ga_{13}Te_{21}O_{66}$ was fixed at 0.9444. The Flack factor for noncentrosymmetric α-$Ga_2(TeO_3)_3$ ($I\bar{4}3d$) was refined as 0.06(4), indicating the correctness of its absolute structure. Ga1 has a large ADP ratio of 5.6; this is probably because of the poor quality of the single crystal as well as the problem with the absorption corrections. Several data sets were collected, but such a problem remained. H atoms associated with aqua ligands in $HLi_2Ga_3(TeO_3)_6(H_2O)_6$ were located at geometrically calculated positions and refined with isotropic thermal parameters. The proton in $HLi_2Ga_3(TeO_3)_6(H_2O)_6$ was necessary for the charge balance, but it is not refined because of the difficulty in determining its exact location; however, we expect that it should be located at one of the six sites with $\bar{3}$ symmetry. Crystallographic data and structural refinements for the compounds are summarized in Table 1. Important bond distances are listed in Table 2. More details on the crystallographic studies as well as atomic displacement parameters are given as Supporting Information.

Results and Discussion

Hydrothermal reactions of Ga_2O_3 [or $Ga(NO_3)_3$], TeO_2, and Li_2CO_3 afforded four new ternary or quaternary gallium tellurites, namely, α-$Ga_2(TeO_3)_3$, β-$Ga_2(TeO_3)_3$, $HLi_2Ga_3(TeO_3)_6(H_2O)_6$, and $Li_9Ga_{13}Te_{21}O_{66}$. It is found that the amount of Li_2CO_3 added is very important to the chemical compositions and structures of the products formed. If 0.10 mmol of Li_2CO_3 was loaded, the noncentrosymmetric α-$Ga_2(TeO_3)_3$ was isolated. When the amount of Li_2CO_3 used was increased to 0.25 mmol, centrosymmetric β-$Ga_2(TeO_3)_3$ was isolated in a very low yield. If we further increase the amount of Li_2CO_3 to 0.35 mmol, $Li_9Ga_{13}Te_{21}O_{66}$ can be isolated. Furthermore, the source of the Ga^{III} ions is also important. Using $Ga(NO_3)_3$ instead of Ga_2O_3 as the gallium source gave another quaternary lithium(I) gallium(III) tellurite(IV), $HLi_2Ga_3(TeO_3)_6(H_2O)_6$. This is probably due to the more acidic reaction media when gallium(III) nitrate is used instead of gallium(III) oxide. The four compounds belong to four different structure types.

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(9) (a) *CrystalClear*, version 1.3.5; Rigaku Corp.: Woodlands, TX, 1999. (b) Sheldrick, G. M. *SHELXTL, Crystallographic Software Package*, version 5.1; Bruker-AXS: Madison, WI, 1998.

(10) (a) Kubelka, P.; Munk, F. *Z. Tech. Phys.* **1931**, *12*, 593. (b) Wendlandt, W. M.; Hecht, H. G. *Reflectance Spectroscopy*; Interscience: New York, 1966.

(11) Kurtz, S. W.; Perry, T. T. *J. Appl. Phys.* **1968**, *39*, 3798.

Table 1. Crystal Data and Structure Refinements for α-$Ga_2(TeO_3)_3$, β-$Ga_2(TeO_3)_3$, $HLi_2Ga_3(TeO_3)_6(H_2O)_6$, and $Li_9Ga_{13}Te_{21}O_{66}$

compound	α-$Ga_2(TeO_3)_3$	β-$Ga_2(TeO_3)_3$	$HLi_2Ga_3(TeO_3)_6(H_2O)_6$	$Li_9Ga_{13}Te_{21}O_{66}$
formula	$Ga_{2/3}TeO_3$	$Ga_2Te_3O_9$	$H_{13}Li_2Ga_3Te_6O_{24}$	$Li_9Ga_{13}Te_{21}O_{66}$
fw	222.08	666.24	1385.74	4704.42
space group	$I\bar{4}3d$ (No. 220)	$P6_3/m$ (No. 176)	$R\bar{3}$ (No. 148)	$R\bar{3}$ (No. 148)
a (Å)	10.528(2)	9.229(2)	9.2149(11)	11.3343(4)
b (Å)	10.528(2)	9.229(2)	9.2149(11)	11.3343(4)
c (Å)	10.528(2)	7.488(2)	25.730(8)	26.799(2)
α (deg)	90	90	90	90
β (deg)	90	90	90	90
γ (deg)	90	120	120	120
V (Å^3)	1167.0(3)	552.4(2)	1892.2(7)	2981.5(2)
Z	16	2	3	2
D_{calc} (g/cm^3)	5.056	4.006	3.648	5.240
μ(Mo Kα) (mm^{-1})	15.983	12.663	10.076	15.987
GOF on F^2	1.070	1.186	1.118	1.191
Flack factor	0.06(4)			
R1, wR2 [$I > 2\sigma(I)$]^a	0.0102, 0.0329	0.0544, 0.1340	0.0353, 0.0847	0.0296, 0.0697
R1, wR2 (all data)^a	0.0102, 0.0329	0.0545, 0.1341	0.0450, 0.0903	0.0317, 0.0707

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = \{\sum w[(F_o)^2 - (F_c)^2]^2/\sum w[(F_o)^2]^2\}^{1/2}$.

α-$Ga_2(TeO_3)_3$ is a noncentrosymmetric compound ($I\bar{4}3d$) exhibiting a moderately strong SHG response, whereas β-$Ga_2(TeO_3)_3$ is centrosymmetric ($P6_3/m$).

Interestingly, α-$Ga_2(TeO_3)_3$ is isostructural to the scintillation crystal $Bi_4Ge_3O_{12}$ (BGO), although their molecular formulas appear different.[12] This is because the Ga^{III} site corresponds to the Ge^{IV} site, whereas Te^{IV} is in the site of the Bi^{III} ion.

The asymmetric unit of α-$Ga_2(TeO_3)_3$ contains one unique Ga atom in the $\bar{4}$ site, one unique Te^{IV} in the 3 site, and one unique O atom in the general site. Ga1 is tetrahedrally coordinated by four tellurite O atoms. The four Ga−O distances are 1.844(3) Å. The Te1 atom is in a ψ-TeO_3 trigonal-pyramidal geometry, with the lone-pair electrons occupying the pyramidal site. The three Te−O distances are 1.887(3) Å. Bond-valence calculations indicate that the Ga and Te atoms are in oxidation states of 3+ and 4+, respectively. The calculated total bond valences for Ga1 and Te1 are 2.94 and 3.82, respectively.[13]

The structure of α-$Ga_2(TeO_3)_3$ features close packing of a three-dimensional (3D) network alternatively connected by GaO_4 tetrahedra and TeO_3 trigonal pyramids via corner sharing (Figure 1a). The $Te1O_3$ group serves as a tridentate metal linker, bridging with three Ga1 atoms. Each GaO_4 tetrahedron is bridged to four TeO_3 groups. Hence, TeO_3 and GaO_4 polyhedra act as 3- and 4-connected nodes, respectively; the 3D structure of α-$Ga_2(TeO_3)_3$ can also be described as a (3,4)-connected double-nodal network in a topological view with the Schläfli symbol of $(8^3)4.(8^6)3$.[14] It exhibits a cubic C_3N_4 (ctn) type topology (Figure 1b).[15] It is also worth comparing the structure of α-$Ga_2(TeO_3)_3$ with that of $Se_2B_2O_7$.[6a] In the structure of $Se_2B_2O_7$, a pair of BO_4 tetrahedra form a $B_2O_7^{8-}$ dimer via corner sharing, whereas no dimerization of the GaO_4 tetrahedra occurred in α-$Ga_2(TeO_3)_3$. Each $B_2O_7^{8-}$ unit connects with six SeO_3 groups, and each SeO_3 group is bridged to three $B_2O_7^{8-}$ units in $Se_2B_2O_7$. Hence, the topological structure of $Se_2B_2O_7$ is a (3,6)-connected double-nodal network in a topological view with the Schläfli symbol of $(4.6^2)2(4^2.6^{10}.8^3)$.[14] The structure of $Se_2B_2O_7$ can be described as a rutile (rtl) network.[16]

β-$Ga_2(TeO_3)_3$ is centrosymmetric ($P6_3/m$), and its structure features a 3D open framework with one-dimensional (1D) 12-MR tunnels along the c axis (Figure 2a). The asymmetric unit of β-$Ga_2(TeO_3)_3$ contains one unique Ga atom in a site of 3-fold axis symmetry, one unique Te^{IV} in the mirror site, and two unique O atoms (O1 in a mirror site and O2 in a general site). Ga1 is octahedrally coordinated with six O atoms. The Ga−O bond distances are in the range of 1.966(9)−2.064(9) Å, which are much longer than those of α-$Ga_2(TeO_3)_3$ in which the Ga^{III} is tetrahedrally coordinated. The trans O−Ga−O angle is 167.6(4)°, whereas the cis O−Ga−O bond angles are in the range of 79.8(4)−96.9(4)°. Hence, the GaO_6 octahedron is slightly distorted. These Ga−O bonds and O−Ga−O angles are comparable to those reported in the other gallium tellurites.[7] The Te^{IV} atom is in a ψ-TeO_3 trigonal-pyramidal geometry, with the lone-pair electrons occupying the pyramidal site. The Te−O distances fall in the range of 1.887(9)−1.896(12) Å. The $Te1O_3$ group is tetradentate, bridging with four Ga1 atoms. O1 is bidentate, whereas O2 is unidentate. Bond-valence calculations indicate that the Ga and Te atoms are in oxidation states of 3+ and 4+, respectively. The calculated total bond valences for Ga1 and Te1 are 2.80 and 3.80, respectively.[13]

Two GaO_6 octahedra are interconnected to a Ga_2O_9 dimer via face sharing; such dimers are bridged by the TeO_3 groups into a 1D gallium tellurite chain along the c axis (Figure 2b). The above chains are further linked by the other TeO_3 groups into a 3D open framework with 1D 12-MR tunnels along the c axis (Figure 2a). The internal diameter of the channel is 7.983 Å (about 0.8 nm). The value provides a crystallographic free diameter of 4.94 Å, which is similar to those of the small-pore zeolites and other molecular sieves such as titanosilicate ETS-4.[17] The framework density (defined as the number of metal atoms for a volume of 1000 Å^3) for β-$Ga_2(TeO_3)_3$ is 15.0, which is close to that of $KGaTe_2O_6 \cdot 1.8H_2O$ (14.6).[7a] The amount of void space is 30% using the CALC SOLV command in *PLATON*.[18] Hence, β-$Ga_2(TeO_3)_3$ is a moderately

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(12) Milenov, T. I.; Rafailov, P. M.; Petrova, R.; Kargin, Y. F.; Gospodinov, M. M. *Mater. Sci. Eng., B* **2007**, *138*, 35.

(13) (a) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244. (b) Brese, N. E.; O'Keeffe, M. *Acta Crystallogr.* **1991**, *B47*, 192.

(14) http://www.topos.ssu.samara.ru: Blatov, V. A. *IUCr CompComm Newsletter* **2006**, *7*, 4.

(15) Dybtsev, D. N.; Chun, H.; Kim, K. *Chem. Commun.* **2004**, *114*, 594.

(16) O'Keeffea, M.; Eddaoudib, M.; Lia, H.; Reinekeb, T.; Yaghi, O. M. *J. Solid State Chem.* **2000**, *152*, 3.

(17) (a) Baerlocher, C.; Meier, W.-M.; Olson, D.-H. *Atlas of Zeolite Structure Types*; Elsevier: Dordrecht, The Netherlands, 2001. (b) Kuznicki, S.-M. Large-pored crystalline titanium molecular sieve zeolites. U.S. Patent 4,853,202, 1989.

(18) Spek, A.-L. *Platon: A Multi-purpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2001.

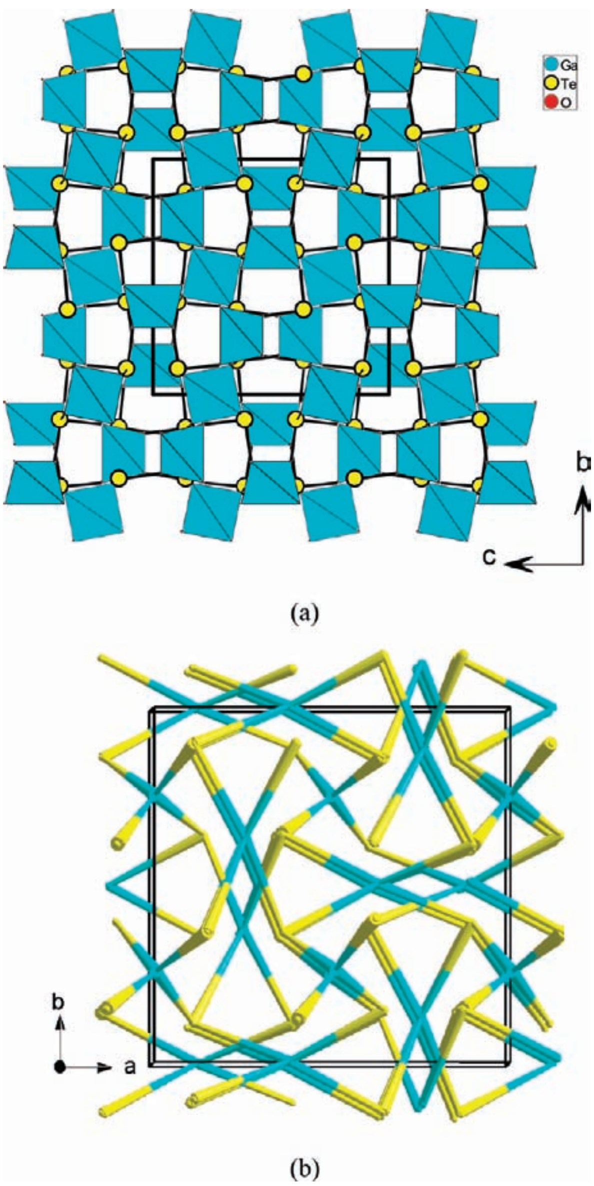
Table 2. Important Bond Lengths (Å) for α-$Ga_2(TeO_3)_3$, β-$Ga_2(TeO_3)_3$, $HLi_2Ga_3(TeO_3)_6(H_2O)_6$, and $Li_9Ga_{13}Te_{21}O_{66}$[a]

	α-$Ga_2(TeO_3)_3$		
Ga1−O1#1	1.844(3)	Ga1−O1#2	1.844(3)
Ga1−O1	1.844(3)	Ga1−O1#3	1.844(3)
Te1−O1	1.887(3)	Te1−O1#4	1.887(3)
Te1−O1#5	1.887(3)		
	β-$Ga_2(TeO_3)_3$		
Ga1−O2#1	1.966(9)	Ga1−O2#2	1.966(9)
Ga1−O2#3	1.966(9)	Ga1−O1	2.064(9)
Ga1−O1#4	2.064(9)	Ga1−O1#5	2.064(9)
Te1−O2	1.887(9)	Te1−O2#6	1.887(9)
Te1−O1	1.896(12)		
	$HLi_2Ga_3(TeO_3)_6(H_2O)_6$		
Li1−O1W	2.015(18)	Li1−O1W#1	2.015(18)
Li1−O1W#2	2.015(18)	Li1−O1#1	2.30(2)
Li1−O1#2	2.30(2)	Li1−O1	2.30(2)
Ga1−O2#3	1.984(5)	Ga1−O2#4	1.984(5)
Ga1−O2#5	1.984(5)	Ga1−O1	1.993(5)
Ga1−O1#1	1.993(5)	Ga1−O1#2	1.993(5)
Ga2−O3#6	1.970(5)	Ga2−O3#7	1.970(5)
Ga2−O3#8	1.970(5)	Ga2−O3#9	1.970(5)
Ga2−O3#10	1.970(5)	Ga2−O3	1.970(5)
Te1−O3	1.864(5)	Te1−O1	1.875(5)
Te1−O2	1.886(5)		
	$Li_9Ga_{13}Te_{21}O_{66}$		
Li1−O8	1.972(13)	Li1−O1#1	1.999(12)
Li1−O3#1	2.038(13)	Li1−O7#2	2.075(12)
Li1−O6#2	2.480(12)	Ga1−O7#3	1.918(4)
Ga1−O7#4	1.918(4)	Ga1−O1	2.013(4)
Ga1−O1#5	2.013(4)	Ga1−O2	2.049(4)
Ga1−O2#5	2.049(4)	Ga2−O5	1.930(1)
Ga2−O8#6	1.974(4)	Ga2−O6#7	1.977(4)
Ga2−O6	2.024(4)	Ga2−O3#8	2.064(4)
Ga2−O4	2.064(5)	Te1−O1#9	1.872(4)
Te1−O1#10	1.872(4)	Te1−O1	1.872(4)
Te2−O4	1.861(4)	Te2−O3	1.873(4)
Te2−O2	1.893(4)	Te3−O8	1.844(4)
Te3−O6	1.887(4)	Te3−O7	1.890(4)

[a] Symmetry transformations used to generate equivalent atoms. α-$Ga_2(TeO_3)_3$: #1, $-x+{}^7/_4, z-{}^1/_4, -y+{}^5/_4$; #2, $x, -y+1, -z+{}^3/_2$; #3, $-x+{}^7/_4, -z+{}^5/_4, y+{}^1/_4$; #4, $-y+1, z-{}^1/_2, -x+{}^3/_2$; #5, $-z+{}^3/_2, -x+1, y+{}^1/_2$. β-$Ga_2(TeO_3)_3$: #1, $x-y+1, x, -z$; #2, $-x+2, -y+1, -z$; #3, $y+1, -x+y+1, -z$; #4, $-x+y+2, -x+2, z$; #5, $-y+2, x-y, z$; #6, $x, y, -z+{}^1/_2$. $HLi_2Ga_3(TeO_3)_6(H_2O)_6$: #1, $-x+y, -x, z$; #2, $-y, x-y, z$; #3, $-x+{}^2/_3, -y+{}^1/_3, -z+{}^1/_3$; #4, $x-y-{}^1/_3, x-{}^2/_3, -z+{}^1/_3$; #5, $y-{}^1/_3, -x+y+{}^1/_3, -z+{}^1/_3$; #6, $y+{}^1/_3, -x+y+{}^2/_3, -z+{}^2/_3$; #7, $x-y+{}^1/_3, x-{}^1/_3, -z+{}^2/_3$; #8, $-x+{}^4/_3, -y+{}^2/_3, -z+{}^2/_3$; #9, $-y+1, x-y, z$; #10, $-x+y+1, -x+1, z$. $Li_9Ga_{13}Te_{21}O_{66}$: #1, $-x+y, -x+1, z$; #2, $-y, x-y+1, z$; #3, $-y+1, x-y+1, z$; #4, $y, -x+y, -z$; #5, $-x+1, -y+1, -z$; #6, $x-y+{}^2/_3, x+{}^1/_3, -z+{}^1/_3$; #7, $-x-{}^1/_3, -y+{}^1/_3, -z+{}^1/_3$; #8, $-y, x-y, z$; #9, $-y+1, x-y, z$; #10, $-x+y+1, -x+1, z$.

strong open-framework structure. In a topological view, TeO_3 and Ga_2O_9 groups can be viewed as 3- and 9-connected nodes, respectively. The structure of β-$Ga_2(TeO_3)_3$ could be described as a (3,9)-connected double-nodal network with the Schläfli symbol of $(4^3)3.(4^{12}.6^{15}.8^9)$ (Figure 2c).[14] Its 3D structure adopts a UCl_3 (gfy) type topology.[19]

Although α-$Ga_2(TeO_3)_3$ and β-$Ga_2(TeO_3)_3$ have chemical formulas similar to that of $Ga_2(TeO_3)_3(H_2O)_3$, their structures are different. $Ga_2(TeO_3)_3(H_2O)_3$ crystallized in the acentric space group $R3c$.[7b] Its asymmetric unit contains two unique Ga^{III}, one TeO_3, and an aqua ligand. One Ga^{III} is octahedrally coordinated by six O atoms from six TeO_3 anions, whereas the other one is octahedrally coordinated by three tellurite anions in a unidentate fashion and three aqua ligands. Each tellurite anion is tridentate and bridges with three Ga^{III} ions. The GaO_6 octahedra are bridged by tellurite anions into a 3D network.



(a)

(b)

Figure 1. View of the polyhedral (a) and topological (b) structures of α-$Ga_2(TeO_3)_3$ along the a axis. GaO_4 tetrahedra are shaded in blue, and Te and O atoms are drawn as yellow and red circles, respectively.

When the amount of Li_2CO_3 used was increased to 0.35 mmol, Li^I was incorporated to form two new quaternary phases, namely, $HLi_2Ga_3(TeO_3)_6(H_2O)_6$ and $Li_9Ga_{13}Te_{21}O_{66}$. They display two types of 3D networks.

The asymmetric unit of $HLi_2Ga_3(TeO_3)_6(H_2O)_6$ contains one unique Li^I atom in the 3 site, two unique Ga^{III} atoms lying on sites of 3 and $\bar{3}$ symmetry, respectively, and one TeO_3 anion and one aqua ligand in the general sites. The proton is not refined, but it should be on one of the $\bar{3}$ sites. Li1 is in a severely distorted octahedral environment, being coordinated by three tellurite anions and three aqua ligands. Three Li−O distances [2.30(2) Å] are much longer than the other three Li−O distances [2.015(18) Å]. Both Ga1 and Ga2 are octahedrally coordinated with six O atoms from six tellurite

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(19) Schleid, T.; Meyer, G.; Morss, L.-R. *J. Less-Common Met.* **1987**, *132*, 69.

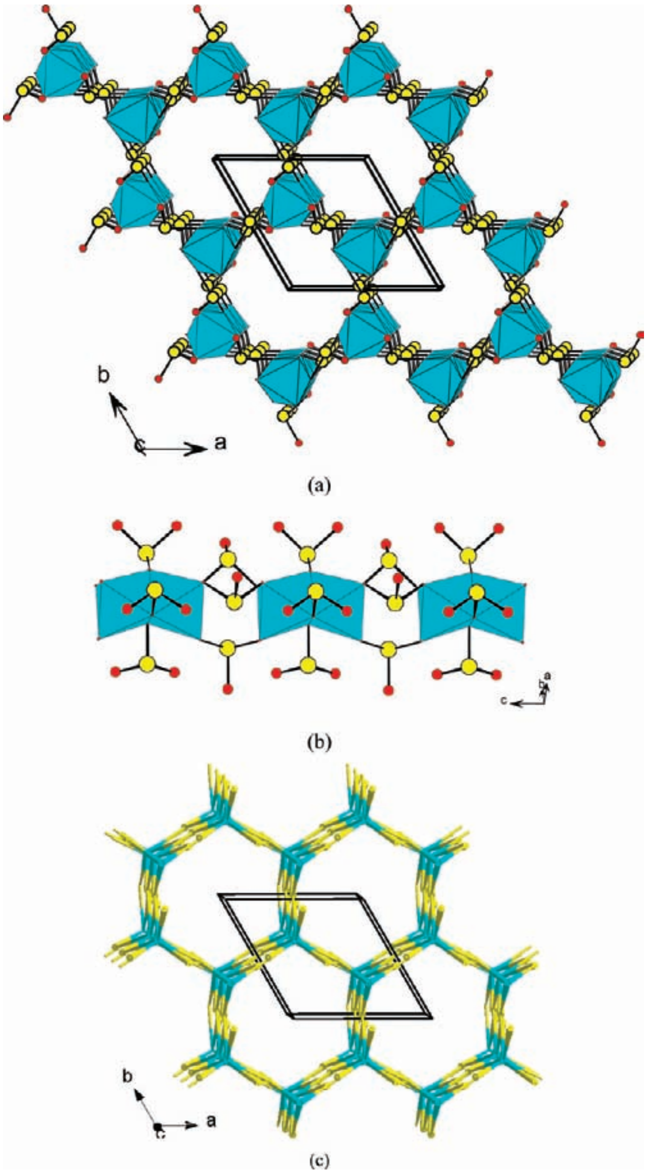

Figure 2. View of the structure of β-$Ga_2(TeO_3)_3$ along the *a* axis (a), a 1D gallium tellurite chain along the *c* axis (b), and a topological view of β-$Ga_2(TeO_3)_3$ along the *c* axis (c). GaO_6 octahedra are shaded in blue, and Te and O atoms are drawn as yellow and red circles, respectively.

anions. The Ga−O band distances are in the range of 1.970(5)−1.993(5) Å. The trans O−Ga−O angles are 174.1(2)−179.999(1)°, whereas the cis O−Ga−O bond angles are in the range of 86.7(2)−93.4(2)°. These Ga−O bonds and O−Ga−O angles are comparable to those reported in the other gallium tellurites.[7] The Te^{IV} atom is in a ψ-TeO_3 trigonal-pyramidal geometry, with the lone-pair electrons occupying the pyramidal site. The distances of Te−O are from 1.864(5) to 1.886(5) Å. The Te1O_3 group is tetradentate, bridging with two Ga1, one Ga2, and one Li1 atoms. Bond-valence calculations indicate that the Ga and Te atoms are in oxidation states of 3+ and 4+, respectively. The calculated total bond valences for Ga1, Ga2, and Te1 are 2.984, 3.137, and 3.953, respectively.[13]

The GaO_6 octahedra are bridged by TeO_3 anions to a 3D network with tunnels of 4- and 8-MRs along the *a* axis (Figure 3b). The Li^I atom and aqua ligands are located at the 8-MR tunnels (Figure 3a). Ga1O_6 octahedra are bridged by Te1O_3 anions to a two-dimensional (2D) gallium tellurite layer running along the $^1/_2$ *c* axis with 12-MRs (Figure 3c). The gallium tellurite layers are further linked by Ga2O_6 octahedra via Te−O−Ga bridges into a 3D framework (Figure 3b). As mentioned earlier, both Ga1 and Ga2 are octahedrally coordinated with six O atoms from six tellurite groups. In a topological view, the Ga1$(TeO_3)_6$ and Ga2-$(TeO_3)_6$ anions can be viewed as 7- and 8-connected nodes, respectively. Hence, the 3D structure of the gallium tellurite could also be described as a (7,8)-connected two-nodal $CaSi_2$ network with the Schläfli symbol of $(3^6.4^{12}.5^6.6^4)(3^6.4^9.5^6)2$ (Figure 3d).[14]

The asymmetric unit of $Li_9Ga_{13}Te_{21}O_{66}$ contains one unique Li atom, two unique Ga atoms (Ga1 in the inversion center and Ga2 in a general site), and three unique Te^{IV} atoms (Te1 on a 3-fold axis and Te2 and Te3 in the general sites). The coordination geometry around Li1 is a distorted square pyramid composed of five O atoms from four tellurite anions, exhibiting a "4 + 1" coordination with four normal [1.972(13)−2.075(12) Å] and one elongated [2.480(12) Å] Li−O bonds. Ga1 is octahedrally coordinated by six O atoms from six tellurite anions, whereas Ga2 is octahedrally coordinated by six O atoms from five tellurite anions and an oxo anion. The bond distances of Ga−O are in the range of 1.918(4)−2.064(5) Å. The trans O−Ga−O angle is 154.87(18)−180.0(3)°, whereas the cis O−Ga−O bond angles are in the range of 75.90(19)−107.41(18)°. These Ga−O bonds and O−Ga−O angles are comparable to those reported in the other gallium tellurites.[7] All of the Te atoms are in a ψ-TeO_3 trigonal-pyramidal geometry, with the lone-pair electrons occupying the pyramidal site. The distances of Te−O are from 1.844(4) to 1.893(4) Å. Bond-valence calculations indicate that the Ga and Te atoms are in oxidation states of 3+ and 4+, respectively. The calculated total bond valences for Ga1, Ga2, Te1, Te2, and Te3 are 2.979, 2.876, 3.984, 3.948, and 3.973, respectively.[13]

$Li_9Ga_{13}Te_{21}O_{66}$ features a complicated anionic 3D framework composed of alternating gallium tellurite layers and Ga2O_6 octahedral layers, with the Li atoms locating at the cavities in the structure (Figure 4a). Ga1O_6 octahedra are bridged by Te1O_3 anions to a 2D layer parallel to the *ab* plane, forming 12-membered polyhedral rings composed of six Ga1O_6 octahedra and six Te1O_3 groups (Figure 4b). A pair of Ga2O_6 octahedra form a Ga_2O_{10} dimer via edge sharing (O6···O6); the dimers are further interconnected by corner sharing into a 2D gallium(III) oxide layer with 12-MRs (Figure 4c). The above two types of layers are alternatively packed along the *c* axis and are interconnected via Ga−O−Te bridges into a 3D network (Figure 4a). No reasonable nodes can be found because the Ga2O_6 octahedra are interconnected to a 2D layer; hence, its topology structure is not be assigned.

IR, UV−Visible Diffuse-Reflectance, and Absorption Spectra. The IR spectra of the four compounds display strong absorption bands between 748 and 683 cm^{-1} of the $(TeO_3)^{2-}$ groups; the vibrations from 545 to 440 cm^{-1} can be assigned to Ga−O bonds.[7] For $HLi_2Ga_3(TeO_3)_6(H_2O)_6$, the stretching vibrations ν(O−H) and bending vibrations ν(H−O−H) of the aqua ligands appear at 3236 and 1610 cm^{-1}, respectively. UV−visible absorption spectra indicate that they are transparent in the range of 300−2500 nm (Figure 5). Optical diffuse-reflectance spectra indicate that α-$Ga_2(TeO_3)_3$, β-$Ga_2(TeO_3)_3$, $HLi_2Ga_3(TeO_3)_6(H_2O)_6$, and $Li_9Ga_{13}Te_{21}O_{66}$ are insulators with optical band gaps of

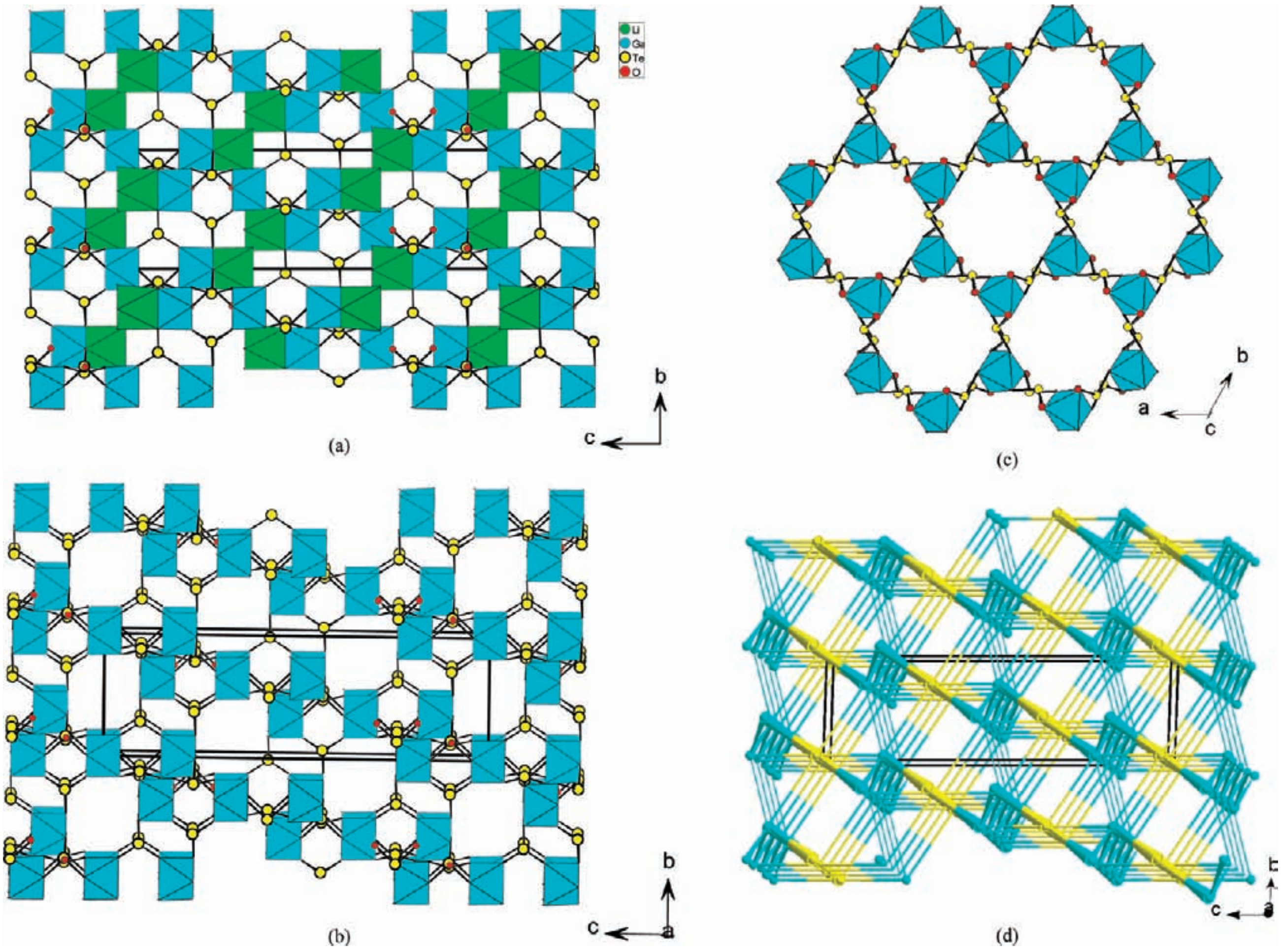

Figure 3. View of the structure of $HLi_2Ga_3(TeO_3)_6(H_2O)_6$ along the *a* axis (a), the 3D gallium(III) tellurite network with 4- and 8-MR tunnels (b), the 2D gallium tellurite layer with 12-MRs (c), and a topological view of the 3D gallium(III) tellurite anion network (d). GaO_6 and LiO_6 octahedra are shaded in blue and yellow, respectively, and Te and O atoms are drawn as yellow and red circles, respectively.

4.14, 4.15, 4.52, and 4.45 eV, respectively (see the Supporting Information).

TGA, DTA, and TG−MS Analysis. For α-$Ga_2(TeO_3)_3$, TGA curves exhibit one step of weight loss in the range of 700−1000 °C, which corresponds to the release of three TeO_2 molecules per formula unit. The observed weight loss of 72.0% is close to the calculated value (71.9%; Figure 6a). The DTA diagram of α-$Ga_2(TeO_3)_3$ exhibits a endothermic peak at 679 °C in the heating curve, but no exothermic peak was found in the cooling curve, indicating that α-$Ga_2(TeO_3)_3$ melted incongruently at around 679 °C (Figure S2 in the Supporting Information). This point is also confirmed by the temperature-dependent powder XRD studies (Figure S1 in the Supporting Information). The powder XRD patterns measured below and above the melting point are different, indicating that α-$Ga_2(TeO_3)_3$ decomposed during melting, although no weight loss was observed. β-$Ga_2(TeO_3)_3$ and $Li_9Ga_{13}Te_{21}O_{66}$ are stable up to 760 and 770 °C, respectively. Then they lose weight continuously, which corresponds to evaporation of TeO_2. The total weight losses at 1100 °C are 65.8% and 68.5%, respectively.

$HLi_2Ga_3(TeO_3)_6(H_2O)_6$ exhibits three main steps of weight loss. The first one from 40 to 175 °C corresponds to partial dehydration. The second dehydration step occurred between 230 and 380 °C. The third one above 825 °C corresponds to further decomposition of TeO_2 formed by decomposition. The total weight loss at 1100 °C is 43.2%, and the final residuals were not characterized because of their reaction with the TGA bucket made of Al_2O_3. TG−MS analysis was performed to investigate decomposition of water. The $m/z = 18$ and 17 curves with the same shape were shown between 40 and 380 °C simultaneously, which indicates that the evolved gas is steam (H_2O, $m/z = 18$; HO^-, $m/z = 17$; Figure 6b).

Second-Order NLO Optical Measurements. Because α-$Ga_2(TeO_3)_3$ is acentric, it is worth studying its exhibited SHG properties. SHG measurements on a Q-switched Nd:YAG laser with the sieved powder samples revealed that α-$Ga_2(TeO_3)_3$ displays a moderately strong SHG response equal to KDP. As was previously stated, α-$Ga_2(TeO_3)_3$ is isostructural to the famous scintillation crystal BGO. From the literature, we knew that the SHG signal of BGO is very weak, about 6 times that of SiO_2.[11] According to Halasyamani et al.'s work, both Te^{IV} and Bi^{III} are lone-pair cations that contribute to the SHG efficiency substantially.[20] To gain a better understanding of the structure−property relationship, we also calculated the local dipole moments of the BiO_6 and TeO_3 polyhedra

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(20) Chang, H. Y.; Ok, K.-M.; Kim, J. H.; Halasyamani, P. S. *Inorg. Chem.* **2007**, *46*, 7005.

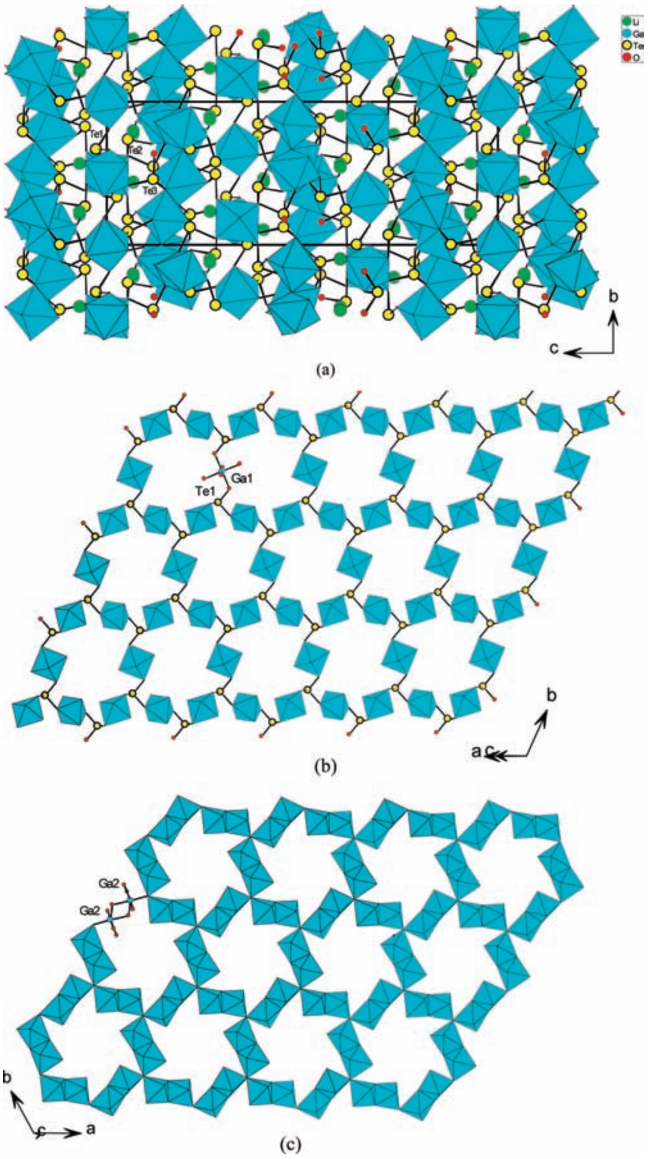

Figure 4. View of the structure of $Li_9Ga_{13}Te_{21}O_{66}$ along the *a* axis (a), a 2D gallium tellurite layer with 12-MRs (b), and a 2D gallium(III) oxide layer with 12-MRs (c). GaO_6 octahedra are shaded in blue, and Li, Te, and O atoms are drawn as green, yellow, and red circles, respectively.

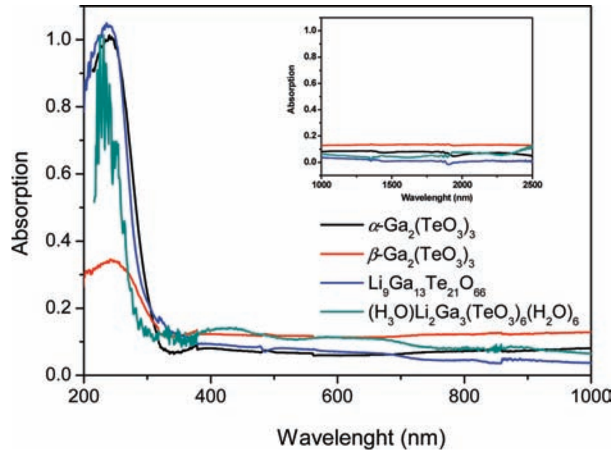

Figure 5. Absorption reflectance spectra for α-$Ga_2(TeO_3)_3$, β-$Ga_2(TeO_3)_3$, $HLi_2Ga_3(TeO_3)_6(H_2O)_6$, and $Li_9Ga_{13}Te_{21}O_{66}$.

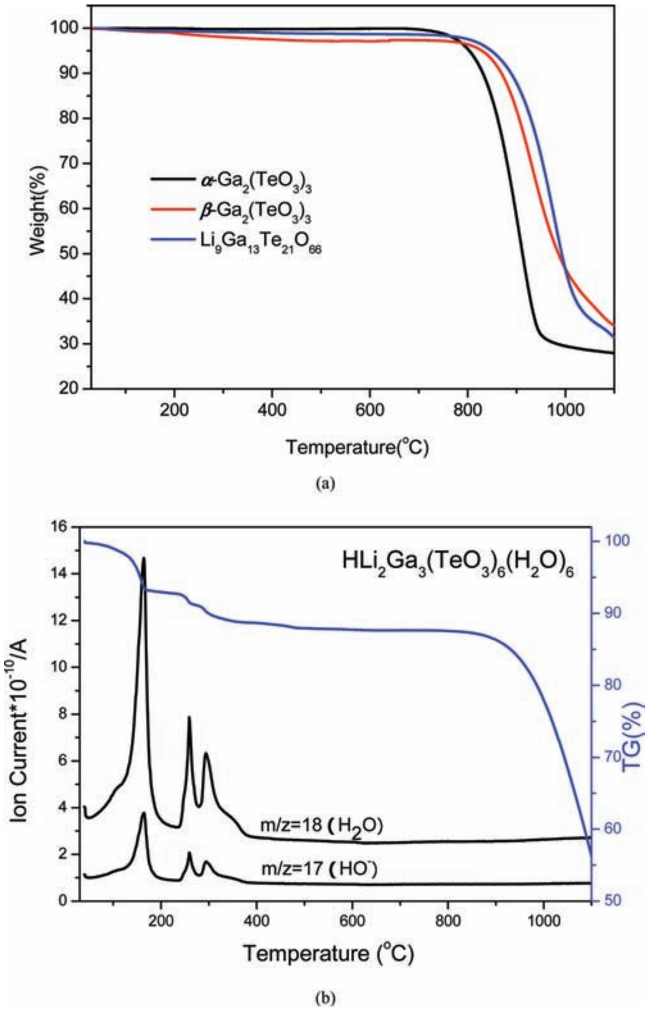

Figure 6. (a) TGA curves for α-$Ga_2(TeO_3)_3$, β-$Ga_2(TeO_3)_3$, and $Li_9Ga_{13}Te_{21}O_{66}$. (b) TG−MS curves of $HLi_2Ga_3(TeO_3)_6(H_2O)_6$.

using the method reported earlier.[21] The lone pairs of the BiO_6 and TeO_3 polyhedra are given a charge of −2 and are located 0.98 and 1.25 Å from the Bi^{III} and Te^{IV} cations, respectively.[22] The calculated magnitude of the dipole moment for BiO_6 polyhedra (6.07 D) is much smaller than that for the TeO_3 polyhedra (11.96 D); this explains why the SHG response of α-$Ga_2(TeO_3)_3$ is much larger than that of BGO.

Conclusions

In summary, four new gallium tellurites(IV), namely, α-$Ga_2(TeO_3)_3$, β-$Ga_2(TeO_3)_3$, $HLi_2Ga_3(TeO_3)_6(H_2O)_6$, and $Li_9Ga_{13}Te_{21}O_{66}$, have been synthesized by hydrothermal reactions. α-$Ga_2(TeO_3)_3$ is noncentrosymmetric and exhibits a moderately strong SHG response. Its structure features close packing of a 3D network alternatively connected by GaO_4 tetrahedra and TeO_3 trigonal pyramids. β-$Ga_2(TeO_3)_3$ is a 3D open-framework structure based on Ga_2O_9 dimers interconnected by TeO_3 groups, forming 1D tunnels of 12-MR. $HLi_2Ga_3(TeO_3)_6(H_2O)_6$ and $Li_9Ga_{13}Te_{21}O_{66}$ represent

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(21) (a) Maggard, P. A.; Nault, T. S.; Stern, C. L.; Poeppelmeier, K. R. *J. Solid State Chem.* **2003**, *175*, 25. (b) Izumi, H. K.; Kirsch, J.; Stern, C. L.; Poeppelmeier, K. R. *Inorg. Chem.* **2005**, *44*, in press.

(22) Galy, J.; Meunier, G. *J. Solid State Chem.* **1975**, *13*, 142.

the first compounds in the $Li^{I}-Ga^{III}-Te^{IV}-O$ system. The structure of $HLi_2Ga_3(TeO_3)_6(H_2O)_6$ can be viewed as the 1D tunnels of the 3D gallium tellurite being occupied by Li^+, H^+, and aqua ligands. $Li_9Ga_{13}Te_{21}O_{66}$ shows a complicated 3D framework composed of alternating gallium tellurite layers and gallium(III) oxide layers with Li^{I} ions located at the voids of the structure. It is found that the amount of Li_2CO_3 used has a dramatic effect on the structures of compounds formed. When only a small amount is used, it acts as only a pH adjuster. However, if the amount used is large enough, Li^+ can be incorporated into the structures as cations. It is expected that a variety of other new compounds with new types of structures and interesting physical properties can be discovered in the metal gallium tellurite or selenite systems by a similar synthetic technique.

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Supporting Information Available: X-ray crystallographic files in CIF format, simulated and experimental powder XRD patterns, DSC curves, and UV−visible optical diffuse-reflectance spectra. This material is available free of charge via the Internet at http://pubs.acs.org.