

# Synthesis, Structure, and Characterization of Novel Two- and Three-Dimensional Vanadates: $\text{Ba}_{2.5}(\text{VO}_2)_3(\text{SeO}_3)_4 \cdot \text{H}_2\text{O}$ and $\text{La}(\text{VO}_2)_3(\text{TeO}_6) \cdot 3\text{H}_2\text{O}$

T. Sivakumar, Kang Min Ok, and P. Shiv Halasyamani\*

Department of Chemistry and Center for Materials Chemistry, University of Houston, 136 Fleming Building, Houston, Texas 77204-5003

Received December 8, 2005

Two new vanadates,  $\text{Ba}_{2.5}(\text{VO}_2)_3(\text{SeO}_3)_4 \cdot \text{H}_2\text{O}$  and  $\text{La}(\text{VO}_2)_3(\text{TeO}_6) \cdot 3\text{H}_2\text{O}$ , have been synthesized by hydrothermal methods using  $\text{BaCO}_3$ ,  $\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$ ,  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{V}_2\text{O}_5$ ,  $\text{TeO}_2$ , and  $\text{H}_2\text{SeO}_3$  as reagents. The structures were determined by single-crystal X-ray diffraction.  $\text{Ba}_{2.5}(\text{VO}_2)_3(\text{SeO}_3)_4 \cdot \text{H}_2\text{O}$  exhibits a two-dimensional layered structure consisting of  $\text{VO}_5$  square pyramids and  $\text{SeO}_3$  polyhedra, whereas  $\text{La}(\text{VO}_2)_3(\text{TeO}_6) \cdot 3\text{H}_2\text{O}$  has a three-dimensional framework structure composed of  $\text{VO}_4$  tetrahedra and  $\text{TeO}_6$  octahedra. Infrared and Raman spectroscopy, UV–vis diffuse reflectance spectroscopy, and thermogravimetric analysis are also presented. Crystal data:  $\text{Ba}_{2.5}(\text{VO}_2)_3(\text{SeO}_3)_4 \cdot \text{H}_2\text{O}$ , trigonal, space group  $\bar{P}3$  (No. 147) with  $a = b = 12.8279(15) \text{ \AA}$ ,  $c = 7.2631(9) \text{ \AA}$ ,  $V = 1035.1(2) \text{ \AA}^3$ , and  $Z = 2$ ;  $\text{La}(\text{VO}_2)_3(\text{TeO}_6) \cdot 3\text{H}_2\text{O}$ , trigonal, space group  $R3c$  (No. 161) with  $a = b = 9.4577(16) \text{ \AA}$ ,  $c = 23.455(7) \text{ \AA}$ ,  $V = 1816.9(7) \text{ \AA}^3$ , and  $Z = 6$ .

## Introduction

Vanadium-based oxides have been attracted considerable attention not only because of the structural versatility<sup>1–6</sup> of vanadium but also their ability to act as intercalation,<sup>7–10</sup> ion-exchange,<sup>11</sup> sorption,<sup>11</sup> magnetic,<sup>12–14</sup> and cathode<sup>15,16</sup>

materials. In vanadates, vanadium has been observed in three-, four-, five-, and six-coordinate environments.<sup>1–6,17</sup> Although vanadium has readily accessible oxidation states, from +2 to +5, tetra- or pentavalent vanadium is observed in the majority of compounds synthesized by hydrothermal reactions.<sup>18–23</sup> In this paper, we report on the hydrothermal synthesis, crystal structure, and characterization of two new vanadates containing not only the tetrahedral or square pyramidal coordination of vanadium with *cis*-dioxovanadium(V) ( $(\text{V}^{5+}\text{O}_2)^+$  vanadyl) moiety but also with different dimensionalities, two-dimensional  $\text{Ba}_{2.5}(\text{VO}_2)_3(\text{SeO}_3)_4 \cdot \text{H}_2\text{O}$  and three-dimensional  $\text{La}(\text{VO}_2)_3(\text{TeO}_6) \cdot 3\text{H}_2\text{O}$ .

## Experimental Section

**Reagents.**  $\text{BaCO}_3$  (Aldrich, 99+%),  $\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$  (Aldrich, 98%),  $\text{La}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  (Aldrich, 99.9%),  $\text{V}_2\text{O}_5$  (Aldrich, 99.6+%),  $\text{TeO}_2$  (Aldrich, 99+%), and  $\text{H}_2\text{SeO}_3$  (Alfa Aesar, 99%) were used as received.

\* To whom correspondence should be addressed: E-mail: psh@uh.edu. Phone: 713-743-3278. Fax: 713-743-0796.

- (1) Wadsley, A. D. *Acta Crystallogr.* **1955**, *8*, 695.
- (2) Nielsen, K.; Fehrmann, R.; Eriksen, K. M. *Inorg. Chem.* **1993**, *32*, 4825.
- (3) Oka, Y.; Saito, F.; Yao, T.; Yamamoto, N. *J. Solid State Chem.* **1997**, *134*, 52.
- (4) Ueda, Y. *Chem. Mater.* **1998**, *10*, 2653.
- (5) Khan, M. I.; Yohannes, E.; Nome, R. C.; Ayes, S.; Golub, V. O.; O'Connor, C. J.; Doedens, R. J. *Chem. Mater.* **2004**, *16*, 5273.
- (6) Kurata, T.; Uehara, A.; Hayashi, Y.; Isobe, K. *Inorg. Chem.* **2005**, *44*, 2524.
- (7) Whittingham, M. S.; Jacobson, A. J. *Intercalation Chemistry*; Academic Press: New York, 1982.
- (8) Jacobson, A. J.; Johnson, J. W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 412.
- (9) Jacobson, A. J.; Johnson, J. W.; Brody, J. F.; Scanlon, J. C.; Lewandowski, J. T. *Inorg. Chem.* **1985**, *24*, 1782.
- (10) Kang, H. Y.; Lee, C. W.; Wang, S. L.; Lii, K. H. *Inorg. Chem.* **1992**, *31*, 4743.
- (11) Kang, H. Y.; Meyer, L. M.; Haushalter, R. C.; Schweitzer, A. L.; Zubieta, L.; Dye, J. L. *Chem. Mater.* **1996**, *8*, 43.
- (12) Papoutsakis, D.; Jackson, J. E.; Nocera, D. G. *Inorg. Chem.* **1996**, *35*, 800.
- (13) Bideau, J. L.; Papoutsakis, D.; Jackson, J. E.; Nocera, D. G. *J. Am. Chem. Soc.* **1997**, *119*, 1313.
- (14) Zhang, Y.; Warren, C. J.; Haushalter, R. C. *Chem. Mater.* **1998**, *10*, 1059.
- (15) Whittingham, M. S. *Mater. Res. Bull.* **1978**, *13*, 959.

- (16) Folkesson, B. *J. Appl. Electrochem.* **1990**, *20*, 907.
- (17) Chirayil, T.; Zavalij, P. Y.; Whittingham, M. S. *Chem. Mater.* **1998**, *10*, 2629.
- (18) Whittingham, M. S.; Guo, J.-D.; Chen, R.; Chirayil, T.; Janauer, G.; Zavalij, P. *Solid State Ionics* **1995**, *75*, 257.
- (19) Oka, Y.; Yao, T. *Nippon Kessho Gakkaiishi* **1998**, *40*, 397.
- (20) Livage, J. *Coord. Chem. Rev.* **1998**, *178–180*, 999.
- (21) Oka, Y.; Yao, T.; Yamamoto, N. *J. Solid State Chem.* **2000**, *152*, 486.
- (22) Dai, Z.; Shi, Z.; Li, G.; Zhang, D.; Fu, W.; Jin, H.; Xu, W.; Feng, S. *Inorg. Chem.* **2003**, *42*, 7396.
- (23) Lutta, S. T.; Chernova, N. A.; Zavalij, P.; Whittingham, M. S. *J. Mater. Chem.* **2004**, *14*, 2922.

**Syntheses.** For  $\text{Ba}_{2.5}(\text{VO}_2)_3(\text{SeO}_3)_4 \cdot \text{H}_2\text{O}$ , 0.4934 g ( $2.5 \times 10^{-3}$  mol) of  $\text{BaCO}_3$ , 0.4547 g ( $2.5 \times 10^{-3}$  mol) of  $\text{V}_2\text{O}_5$ , and 0.7248 g ( $5.62 \times 10^{-3}$  mol) of  $\text{H}_2\text{SeO}_3$  were combined with 10 mL of  $\text{H}_2\text{O}$ . For  $\text{La}(\text{VO}_2)_3(\text{TeO}_6) \cdot 3\text{H}_2\text{O}$ , 0.3249 g ( $1 \times 10^{-3}$  mol) of  $\text{La}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ , 0.1819 g ( $1 \times 10^{-3}$  mol) of  $\text{V}_2\text{O}_5$ , and 0.1596 g ( $1 \times 10^{-3}$  mol) of  $\text{TeO}_2$  were combined with 10 mL of  $\text{H}_2\text{O}$ . The respective solutions were placed in 23-mL Teflon-lined autoclaves and subsequently sealed. The autoclaves were gradually heated to 230–240 °C, held for 2–4 d (for  $\text{Ba}_{2.5}(\text{VO}_2)_3(\text{SeO}_3)_4 \cdot \text{H}_2\text{O}$ , 230 °C for 4 d, and for  $\text{La}(\text{VO}_2)_3(\text{TeO}_6) \cdot 3\text{H}_2\text{O}$ , 240 °C for 2 d) and cooled slowly to room temperature at 6 °C  $\text{h}^{-1}$ . The mother liquor was decanted from the products, and the products were recovered by filtration and washed with distilled water. For  $\text{Ba}_{2.5}(\text{VO}_2)_3(\text{SeO}_3)_4 \cdot \text{H}_2\text{O}$ , light yellow crystals were found in 60% yield based on  $\text{V}_2\text{O}_5$ . For  $\text{La}(\text{VO}_2)_3(\text{TeO}_6) \cdot 3\text{H}_2\text{O}$ , colorless crystals were found in 70% yield based on  $\text{V}_2\text{O}_5$ . For  $\text{Ba}_{2.5}(\text{VO}_2)_3(\text{SeO}_3)_4 \cdot \text{H}_2\text{O}$ , a yield of nearly 90% was obtained by using the above procedure with the reagents  $\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$  (1.542 g,  $8.14 \times 10^{-3}$  mol),  $\text{V}_2\text{O}_5$  (0.8184 g,  $4.5 \times 10^{-3}$  mol), and  $\text{H}_2\text{SeO}_3$  (1.7395 g,  $13.5 \times 10^{-3}$  mol) were combined with 10 mL of  $\text{H}_2\text{O}$  at 240 °C for 4 d.

**Single-Crystal X-ray Diffraction.** For  $\text{Ba}_{2.5}(\text{VO}_2)_3(\text{SeO}_3)_4 \cdot \text{H}_2\text{O}$  a light yellow block ( $0.08 \times 0.19 \times 0.27 \text{ mm}^3$ ) and for  $\text{La}(\text{VO}_2)_3(\text{TeO}_6) \cdot 3\text{H}_2\text{O}$  a colorless block ( $0.10 \times 0.12 \times 0.15 \text{ mm}^3$ ) were used for single-crystal data analyses. Data were collected using a Siemens SMART diffractometer equipped with a 1K CCD area detector using graphite-monochromated Mo  $K\alpha$  radiation. A hemisphere of data was collected using a narrow-frame method with scan widths of 0.30 in. and an exposure time of 25 s per frame. The first 50 frames were remeasured at the end of the data collection to monitor instrument and crystal stability. The maximum correction applied to the intensities was <1%. The data were integrated using the Siemens SAINT program,<sup>24</sup> with the intensities corrected for Lorentz, polarization, air absorption, and absorption attributable to the variation in the path length through the detector faceplate.  $\Psi$ -scans were used for the absorption correction on the hemisphere of data. The data were solved by direct methods using SHELXS-97<sup>25</sup> and refined using SHELXL-97.<sup>26</sup> All of the atoms were refined with anisotropic thermal parameters and converged for  $I > 2(I)$ . All calculations were performed using the WinGX-98 crystallographic software package.<sup>27</sup> Relevant crystallographic data and selected bond distances are given in Tables 1 and 2, respectively.

**Powder X-ray Diffraction.** Powder X-ray diffraction was used to confirm the phase purity of each sample. The X-ray powder diffraction data were collected on a Scintag XDS2000 diffractometer at room temperature (Cu  $K\alpha$  radiation,  $\theta$ - $\theta$  mode, flat plate geometry) equipped with Peltier germanium solid-state detector in the  $2\theta$  range 5–60° with a step size of 0.02 and a step time of 10 s.

**Infrared and Raman Spectroscopy.** Infrared spectra were recorded on a Matteson FTIR 5000 spectrometer in the 400–4000  $\text{cm}^{-1}$  range with the sample pressed between two KBr pellets. Raman spectra were recorded at room temperature under the control of Spex DM3000 microcomputer system using a conventional scanning Raman instrument equipped with a Spex 1403 double monochromator (with a pair of 1800 grooves/mm gratings) and a Hamamatsu 928 photomultiplier detector. The powder samples were

**Table 1.** Crystallographic Data for  $\text{Ba}_{2.5}(\text{VO}_2)_3(\text{SeO}_3)_4 \cdot \text{H}_2\text{O}$  and  $\text{La}(\text{VO}_2)_3(\text{TeO}_6) \cdot 3\text{H}_2\text{O}$

formula	$\text{Ba}_{2.5}(\text{VO}_2)_3(\text{SeO}_3)_4 \cdot \text{H}_2\text{O}$	$\text{La}(\text{VO}_2)_3(\text{TeO}_6) \cdot 3\text{H}_2\text{O}$
fw	1117.99	665.33
space group	$P\bar{3}$ (No. 147)	$R\bar{3}c$ (No. 161)
<i>a</i> (Å)	12.8279(15)	9.4577(16)
<i>b</i> (Å)	12.8279(15)	9.4577(16)
<i>c</i> (Å)	7.2631(9)	23.455(7)
$\alpha$ (°)	90	90
$\beta$ (°)	90	90
$\gamma$ (°)	120	120
<i>V</i> (Å <sup>3</sup> )	1035.1(2)	1816.9(7)
<i>Z</i>	2	6
<i>T</i> (°C)	293.0(2)	293.0(2)
$\lambda$ (Å)	0.71073	0.71073
$\rho_{\text{calcd}}$ (g $\text{cm}^{-3}$ )	3.601	3.616
$\mu$ ( $\text{mm}^{-1}$ )	13.53	8.139
<i>R</i> ( <i>F</i> ) <sup>a</sup>	0.0585	0.0252
<i>R</i> <sub>w</sub> ( <i>F</i> <sub>o</sub> <sup>2</sup> ) <sup>b</sup>	0.1894	0.0932

$$^a R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w(F_o^2) = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

**Table 2.** Selected Bond Distances (Å) for  $\text{Ba}_{2.5}(\text{VO}_2)_3(\text{SeO}_3)_4 \cdot \text{H}_2\text{O}$  and  $\text{La}(\text{VO}_2)_3(\text{TeO}_6) \cdot 3\text{H}_2\text{O}$

	$\text{Ba}_{2.5}(\text{VO}_2)_3(\text{SeO}_3)_4 \cdot \text{H}_2\text{O}$	$\text{La}(\text{VO}_2)_3(\text{TeO}_6) \cdot 3\text{H}_2\text{O}$	
Se1–O1 × 3	1.708(9)	Te1–O1 × 3	1.916(6)
Se2–O2	1.724(9)	Te1–O2 × 3	1.895(6)
Se2–O3	1.711(9)	V1–O1	1.800(6)
Se2–O4	1.651(9)	V1–O2	1.847(6)
V1–O1	2.006(9)	V1–O3 (V=O)	1.632(6)
V1–O2	1.952(8)	V1–O4 (V=O)	1.643(6)
V1–O3	1.981(9)		
V1–O5 (V=O)	1.642(9)		
V1–O6 (V=O)	1.647(9)		

placed in separate capillary tubes during the experiment. Excitation was provided by a coherent Ar<sup>+</sup> ion laser at a wavelength of 457 nm with 100 mW laser power and 4  $\text{cm}^{-1}$  slit widths.

**UV–Vis Diffuse Reflectance Spectroscopy.** UV–vis diffuse reflectance data for all of the reported compounds were collected on a Varian Cary 500 scan UV–vis–NIR spectrophotometer over the spectral range 300–1500 nm at room temperature. Poly-(tetrafluoroethylene) was used as a reference material. Reflectance spectra were converted to absorbance with the Kubelka–Munk values.<sup>28</sup>

**Thermogravimetric Analysis (TGA).** Thermogravimetric analyses were carried out on a TGA 2050 thermogravimetric analyzer (TA instruments). The sample was contained within a platinum crucible and heated in oxygen at a rate of 5 °C  $\text{min}^{-1}$  to 1000 °C.

## Results and Discussion

**Structures.**  $\text{Ba}_{2.5}(\text{VO}_2)_3(\text{SeO}_3)_4 \cdot \text{H}_2\text{O}$  exhibits a two-dimensional layered structure consisting of layers of  $\text{VO}_5$  square pyramids linked to  $\text{SeO}_3$  polyhedra in which the  $\text{Ba}^{2+}$  cations and  $\text{H}_2\text{O}$  molecules occupy the interlayer region (see Figure 1). Interestingly, each layer consists of eclipsed 12-membered rings constructed from  $\text{VO}_5$  square pyramids and  $\text{SeO}_3$  polyhedra. These 12-membered rings are surrounded by smaller eight-membered rings, and the water molecule resides in the middle of the 12-membered rings (see Figure 2). The dehydration of water molecule leads to 12-MR channels ( $\sim 9.7 \times 7.0$  Å) that are surrounded by 8-MR channels ( $\sim 8.7 \times 2.3$  Å). No structural change is observed after dehydration. Each  $\text{V}^{5+}$  is bonded to five oxygen atoms in a distorted square pyramidal environment with two “short” (1.642(9) and 1.647(9) Å) and three “normal” bonds (1.952–

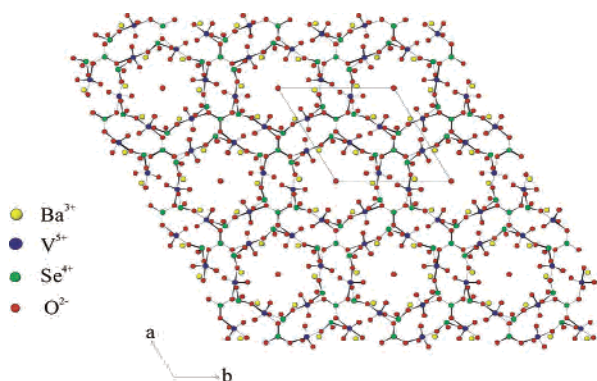
(24) SAINT, v. Program for Area Detector Absorption Correction; Siemens Analytical X-ray Instruments: Madison, WI, 1995.

(25) Sheldrick, G. M. SHELXS-97-A program for automatic solution of crystal structures; University of Göttingen: Göttingen, Germany, 1997.

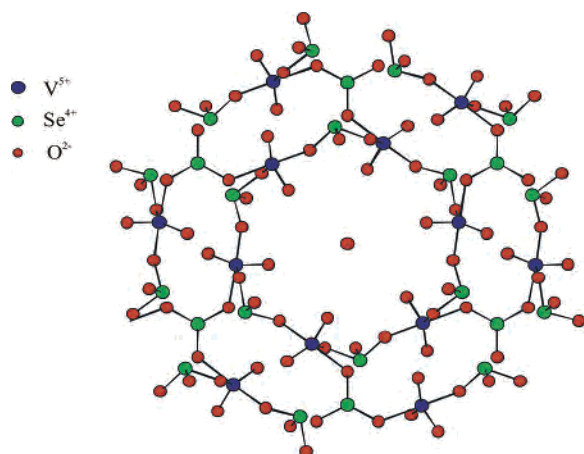
(26) Sheldrick, G. M. SHELXL-97-A program for crystal structure refinement; University of Göttingen: Göttingen, Germany, 1997.

(27) Farrugia, L. J. J. Appl. Crystallogr. **1999**, 32, 837.

(28) Kubelka, P.; Munk, F. Z. Tech. Phys. **1931**, 12, 593.



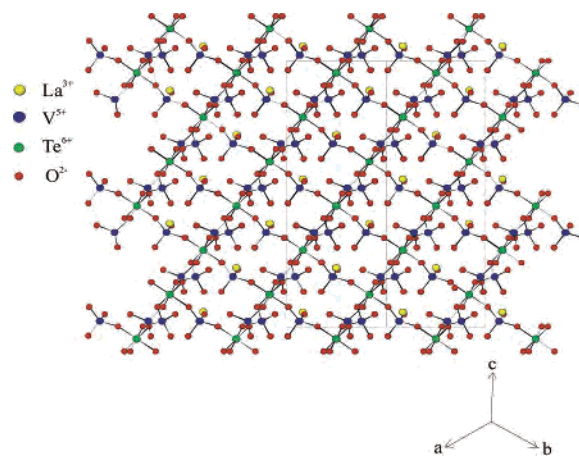
**Figure 1.** Ball-and-stick diagram of  $\text{Ba}_{2.5}(\text{VO}_2)_3(\text{SeO}_3)_4 \cdot \text{H}_2\text{O}$  in the  $ab$  plane. Note the 12-membered rings that are surrounded by 8-membered rings.



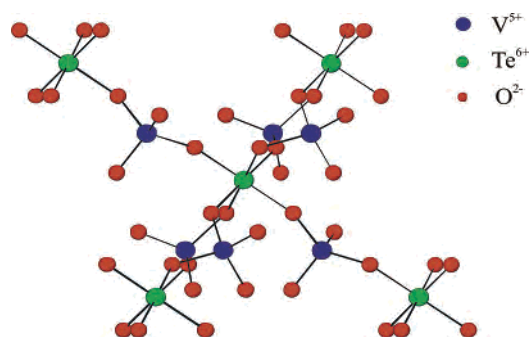
**Figure 2.** Ball-and-stick representation of the 12- and 8-membered rings in  $\text{Ba}_{2.5}(\text{VO}_2)_3(\text{SeO}_3)_4 \cdot \text{H}_2\text{O}$ .

(8)–2.006(9) Å). Three of the five oxygen atoms are further bonded to  $\text{Se}^{4+}$  cations, whereas the two “short” V–O bonds remain terminal. The two unique  $\text{Se}^{4+}$  cations ( $\text{Se}(1)^{4+}$  and  $\text{Se}(2)^{4+}$ ) are bonded to three oxygen atoms. All three oxygen atoms of  $\text{Se}(1)^{4+}$  are further bonded to  $\text{V}^{5+}$ , whereas in  $\text{Se}(2)^{4+}$ , two of the three oxygen atoms are further bonded to  $\text{V}^{5+}$ , the “short”  $\text{Se}(2)$ –O bond (1.651(9) Å) remains terminal. In connectivity terms, the structure may be written as  $[(3(\text{VO}_{3/2}\text{O}_{2/1})^{2-}(\text{SeO}_{3/2})^{2+}3(\text{SeO}_{2/2}\text{O}_{1/1})^0)]^{5-}$  with charge balance maintained by the interlayer cation,  $\text{Ba}^{2+}$ . Bond valence calculations<sup>29</sup> resulted in values of 1.90 for  $\text{Ba}^{2+}$ , 3.96 for  $\text{Se}(1)^{4+}$ , 4.12 for  $\text{Se}(2)^{4+}$ , and 4.93 for  $\text{V}^{5+}$ .

$\text{La}(\text{VO}_2)_3(\text{TeO}_6) \cdot 3\text{H}_2\text{O}$  exhibits a three-dimensional framework structure consisting of  $\text{VO}_4$  tetrahedra and  $\text{TeO}_6$  octahedra that are separated by  $\text{La}^{3+}$  cations and  $\text{H}_2\text{O}$  molecules that reside in the tunnels (see Figure 3). Each  $\text{V}^{5+}$  is bonded to four oxygen atoms in a distorted tetrahedral environment with two “short” (1.632(6) and 1.643(6) Å) and two “normal” bonds (1.800(6) and 1.847(6) Å). Two of the four oxygen atoms are further bonded to a  $\text{Te}^{6+}$  cation, whereas the two short V–O bonds remain terminal (see Figure 4). In connectivity terms, the structure may be written as  $[3(\text{VO}_{2/2}\text{O}_{2/1})^{2-}(\text{TeO}_6)^0]^{3-}$  with charge balance maintained by the  $\text{La}^{3+}$  cation. Each  $\text{Te}^{6+}$  is bonded to six oxygen atoms in a nearly regular octahedral environment with Te–O bond



**Figure 3.** Ball-and-stick representation of the three-dimensional  $\text{La}(\text{VO}_2)_3(\text{TeO}_6) \cdot 3\text{H}_2\text{O}$  is shown. The water molecules have been removed for clarity.



**Figure 4.** Ball-and-stick representation of the  $\text{TeO}_6$  and  $\text{VO}_4$  polyhedra in  $\text{La}(\text{VO}_2)_3(\text{TeO}_6) \cdot 3\text{H}_2\text{O}$ . Note that each  $\text{TeO}_6$  polyhedron is surrounded by six  $\text{VO}_4$  tetrahedra.

distances ranging from 1.895(6) to 1.916(6) Å. All six oxygen atoms are further bonded to  $\text{V}^{5+}$  cation (see Figure 4). Bond valence calculations<sup>29</sup> resulted in values of 3.26 for  $\text{La}^{3+}$ , 6.19 for  $\text{Te}^{6+}$ , and 5.02 for  $\text{V}^{5+}$ .  $\text{La}(\text{VO}_2)_3(\text{TeO}_6) \cdot 3\text{H}_2\text{O}$  is acentric, crystallizing in the noncentrosymmetric (NCS) space group  $R3c$ . Powder SHG measurements were performed, however, the SHG efficiency is below the detection limit of our instrument.<sup>30</sup> In this material, the two metal oxide polyhedra that could contribute to the SHG are the  $\text{V}^{5+}\text{O}_4$  tetrahedra and the  $\text{Te}^{6+}\text{O}_6$  octahedra. With the former, the tetrahedral coordination of  $\text{V}^{5+}$ , although inherently NCS (chiral but not polar), are not aligned macroscopically, whereas with the latter,  $\text{Te}^{6+}$ , similar to  $\text{Sn}^{4+}$  and  $\text{Sb}^{5+}$ , does not undergo a substantial distortion from the center of its oxide octahedron. Thus, both the  $\text{VO}_4$  and  $\text{TeO}_6$  polyhedra contribute minimally to any possible SHG, resulting in a very weak response.

Significantly, both of the vanadium polyhedra (distorted  $\text{VO}_5$  square pyramid and distorted  $\text{VO}_4$  tetrahedra) in the two reported structures, two-dimensional  $\text{Ba}_{2.5}(\text{VO}_2)_3(\text{SeO}_3)_4 \cdot \text{H}_2\text{O}$  and three-dimensional  $\text{La}(\text{VO}_2)_3(\text{TeO}_6) \cdot 3\text{H}_2\text{O}$ , exhibit a dioxovanadium(V) ( $(\text{V}^{5+}\text{O}_2)^+$  vanadyl) feature attributable to the short terminal V–O bonds ( $\text{V}=\text{O}$ ). The short V–O bond distances (1.63–1.65 Å) are consistent with those of reported values (1.62–1.67 Å) in the literature.<sup>31,32</sup> In

(29) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244.

(30) Porter, Y.; Ok, K. M.; Halasyamani, P. S. *Chem. Mater.* **2001**, *13*, 1910.

(31) Sykora, R. E.; Ok, K. M.; Halasyamani, P. S.; Wells, D. M.; Albrecht-Schmitt, T. E. *Chem. Mater.* **2002**, *14*, 2741.



**Table 3.** Infrared and Raman Vibrations (cm<sup>-1</sup>) for Ba<sub>2.5</sub>(VO<sub>2</sub>)<sub>3</sub>(SeO<sub>3</sub>)<sub>4</sub>·H<sub>2</sub>O and La(VO<sub>2</sub>)<sub>3</sub>(TeO<sub>6</sub>)·3H<sub>2</sub>O

Ba <sub>2.5</sub> (VO <sub>2</sub> ) <sub>3</sub> (SeO <sub>3</sub> ) <sub>4</sub> ·H <sub>2</sub> O				La(VO <sub>2</sub> ) <sub>3</sub> (TeO <sub>6</sub> )·3H <sub>2</sub> O			
V=O	V-O	Se-O	O-H	V=O	V-O	Te-O	O-H
IR							
963	863	759	3494	962	884	737	3433
934	915	740	1622	949	792	565	1620
910	496	657		938	505		
		558		912			
		536					
		470					
Raman							
959	857	756		966	884	781	
939	827	728		958	859	718	
913	809	677		942	794	648	
	447	620		908	494		
	409	534			441		
		487					

addition, the dioxovanadium(V) unit in all of the reported compounds adopt a cis configuration (O=V=O) with O–V–O bond angle ranging from 105 to 107° (∠O–V–O in the VO<sub>5</sub> square pyramid of Ba<sub>2.5</sub>(VO<sub>2</sub>)<sub>3</sub>(SeO<sub>3</sub>)<sub>4</sub>·H<sub>2</sub>O is 105.9(5)°, and ∠O–V–O in the VO<sub>4</sub> tetrahedra of La(VO<sub>2</sub>)<sub>3</sub>(TeO<sub>6</sub>)·3H<sub>2</sub>O is 106.8(3)°). Infrared, Raman, and UV–vis diffuse reflectance spectroscopy data also confirm the VO<sub>2</sub><sup>+</sup> vanadyl feature.

**Infrared and Raman Spectroscopy.** The infrared and Raman spectra of Ba<sub>2.5</sub>(VO<sub>2</sub>)<sub>3</sub>(SeO<sub>3</sub>)<sub>4</sub>·H<sub>2</sub>O and La(VO<sub>2</sub>)<sub>3</sub>(TeO<sub>6</sub>)·3H<sub>2</sub>O reveal the presence of a VO<sub>2</sub><sup>+</sup> vanadyl unit attributable to the V=O (short terminal V–O bonds) vibrations in the region ca. 900–970 cm<sup>-1</sup> and V–O vibrations in the region ca. 700–900 cm<sup>-1</sup>. The stretches 781–565 and 759–470 cm<sup>-1</sup> can be attributed to Te–O and Se–O vibrations, respectively. The infrared and Raman vibrations and their assignments are listed in Table 3. The assignments are consistent with those previously reported.<sup>31–40</sup>

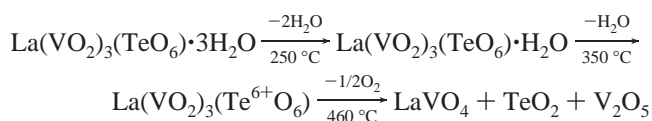
**UV–Vis Diffuse Reflectance Spectroscopy.** The UV–vis diffuse reflectance spectra for the title compounds have been deposited in the Supporting Information. Ba<sub>2.5</sub>(VO<sub>2</sub>)<sub>3</sub>(SeO<sub>3</sub>)<sub>4</sub>·H<sub>2</sub>O is yellow, whereas La(VO<sub>2</sub>)<sub>3</sub>(TeO<sub>6</sub>)·3H<sub>2</sub>O is yellow-green (La(VO<sub>2</sub>)<sub>3</sub>(TeO<sub>6</sub>) is yellow). These spectra show that the absorption is approximately 2.2–2.7 eV. Absorption (*K/S*) data were calculated from the following Kubelka–Munk function:<sup>28</sup>

$$F(R) = \frac{(1 - R)^2}{2R} = \frac{K}{S}$$

with *R* representing the reflectance, *K* the absorption, and *S* the scattering. In a *K/S* vs *E* (eV) plot, extrapolating the linear part of the rising curve to zero provides the onset of

absorption at 2.7 and 2.2 eV for Ba<sub>2.5</sub>(VO<sub>2</sub>)<sub>3</sub>(SeO<sub>3</sub>)<sub>4</sub>·H<sub>2</sub>O and La(VO<sub>2</sub>)<sub>3</sub>(TeO<sub>6</sub>)·3H<sub>2</sub>O, respectively. The onset is attributed by the absorption of light in approximately the green region due to (V<sup>5+</sup>O<sub>2</sub>)<sup>+</sup> vanadyl units. It is likely that the visible absorption in the reported compounds can be attributed to charge transfer in the vanadyl units. The onset of absorption values for the reported compounds is in good agreement with the previous study of compounds containing VO<sub>2</sub><sup>+</sup> vanadyl units such as vanadyl iodates<sup>31</sup> and vanadyl tellurate.<sup>32</sup>

**Thermogravimetric Analysis.** Both Ba<sub>2.5</sub>(VO<sub>2</sub>)<sub>3</sub>(SeO<sub>3</sub>)<sub>4</sub>·H<sub>2</sub>O and La(VO<sub>2</sub>)<sub>3</sub>(TeO<sub>6</sub>)·3H<sub>2</sub>O decompose at 340 and 460 °C, respectively. The TGA curve of Ba<sub>2.5</sub>(VO<sub>2</sub>)<sub>3</sub>(SeO<sub>3</sub>)<sub>4</sub>·H<sub>2</sub>O shows a continuous decomposition up to 770 °C with a plateau around 350 °C attributable to the loss of H<sub>2</sub>O followed by the sublimation of SeO<sub>2</sub>: calcd(exptl) 41.40%–(37.87%). Dehydration of Ba<sub>2.5</sub>(VO<sub>2</sub>)<sub>3</sub>(SeO<sub>3</sub>)<sub>4</sub>·H<sub>2</sub>O, at 340 °C for 1 h (calcd(exptl) 1.61% (1.70%)) yields anhydrous Ba<sub>2.5</sub>(VO<sub>2</sub>)<sub>3</sub>(SeO<sub>3</sub>)<sub>4</sub> and occurs isostructurally as revealed by powder XRD (see Figure S5, Supporting Information). However, the nitrogen adsorption isotherm for Ba<sub>2.5</sub>(VO<sub>2</sub>)<sub>3</sub>(SeO<sub>3</sub>)<sub>4</sub> indicates nonporous behavior (see Figure S12, Supporting Information). The TGA curve of La(VO<sub>2</sub>)<sub>3</sub>(TeO<sub>6</sub>)·3H<sub>2</sub>O reveals a weight loss between 150 and 250 °C attributable to the loss of 2 mol of H<sub>2</sub>O molecules: calcd(exptl) 5.41% (5.16%). At around 350 °C, an additional mole of H<sub>2</sub>O is lost, resulting in the formation of anhydrous La(VO<sub>2</sub>)<sub>3</sub>(TeO<sub>6</sub>): calcd(exptl) 2.86% (2.34%). The anhydrous La(VO<sub>2</sub>)<sub>3</sub>(TeO<sub>6</sub>) could also be indexed in *R3c* space group with *a* = *b* = 9.256(5) Å (2.1% reduced), *c* = 22.79(2) Å (2.8% reduced), and *V* = 1691(2) Å<sup>3</sup> (see Figure S6 and Table S1, Supporting Information), revealing that the structure of anhydrous La(VO<sub>2</sub>)<sub>3</sub>(TeO<sub>6</sub>) is similar to the hydrated phase La(VO<sub>2</sub>)<sub>3</sub>(TeO<sub>6</sub>)·3H<sub>2</sub>O. At 460 °C, the loss of 1 mol of oxygen from La(VO<sub>2</sub>)<sub>3</sub>(TeO<sub>6</sub>) results in the formation of LaVO<sub>4</sub>: calcd(exptl) 2.62% (2.42%). The reactions occurring during the heating of La(VO<sub>2</sub>)<sub>3</sub>(TeO<sub>6</sub>)·3H<sub>2</sub>O may be written as



The TGA curves for both of the materials have been deposited in the Supporting Information.

**Acknowledgment.** We thank the Robert A. Welch Foundation for support. This work was also supported by the NSF-Career Program through Grant No. DMR-0092054 and by the NSF-Chemical Bonding Center. We also acknowledge Prof. R. Czernuszewicz for assistance in obtaining the Raman spectra.

**Supporting Information Available:** X-ray crystallographic files for Ba<sub>2.5</sub>(VO<sub>2</sub>)<sub>3</sub>(SeO<sub>3</sub>)<sub>4</sub>·H<sub>2</sub>O and La(VO<sub>2</sub>)<sub>3</sub>(TeO<sub>6</sub>)·3H<sub>2</sub>O in CIF format; ORTEP diagrams, experimental and observed powder XRD patterns, IR spectra, Raman spectra, UV–vis diffuse reflectance curves, nitrogen adsorption isotherm for the dehydrated material, and TGA curves for two reported materials. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC052103U

- (32) Sullens, T. A.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2005**, *44*, 2282.  
 (33) Frost, R. L.; Erickson, K. L.; Weier, M. L.; Carmody, O. *Spectrochim. Acta* **2005**, *61A*, 829.  
 (34) Devi, R. N.; Vidyasagar, K. J. *Chem. Soc., Dalton Trans.* **1998**, 3013.  
 (35) Ok, K. M.; Halasyamani, P. S. *Chem. Mater.* **2002**, *14*, 2360.  
 (36) Ok, K. M.; Halasyamani, P. S. *Inorg. Chem.* **2004**, *43*, 4248.  
 (37) Vaughey, J. T.; Harrison, W. T. A.; Dussack, L. L.; Jacobson, A. J. *Inorg. Chem.* **1994**, *33*, 4370.  
 (38) Zheng, S.-T.; Zhang, J.; Yang, G.-Y. *Inorg. Chem.* **2005**, *44*, 2426.  
 (39) Yu, R.; Ok, K. M.; Halasyamani, P. S. *Dalton Trans.* **2004**, 392.  
 (40) Frost, R. L.; Erickson, K.; Weier, M. L. *Spectrochim. Acta* **2004**, *60A*, 2419.