

Hydrothermal Synthesis of Lanthanum Vanadates: Synthesis and Crystal Structures of Zircon-Type LaVO_4 and a New Compound LaV_3O_9

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In the course of hydrothermal synthesis of lanthanum vanadates, zircon-type LaVO_4 and LaV_3O_9 have been obtained and structurally characterized. The former is a metastable phase, and the latter is a new compound. Single-crystal X-ray diffractometry confirmed the zircon-type structure for LaVO_4 : $I4_1/amd$ with $a = 7.4578(7)$ Å, $c = 6.5417(9)$ Å, and $Z = 4$; $R = 0.020$ and $R_w = 0.025$ for 276 reflections with $I > 3\sigma(I)$. The structure consists of isolated VO_4 tetrahedra which surround the La atom to form a LaO_8 dodecahedron. LaV_3O_9 adopts the monoclinic system: $P2_1/m$ with $a = 4.949(2)$ Å, $b = 9.547(3)$ Å, $c = 7.411(2)$ Å, $\beta = 100.76(2)^\circ$, and $Z = 2$; $R = 0.035$ and $R_w = 0.042$ for 1868 reflections with $I > 3\sigma(I)$. The structure adopts a chain-type one consisting of a V_3O_9 chain along $[010]$ which is made up of edge-sharing VO_5 trigonal-bipyramid pairs and VO_4 tetrahedra. The La atom resides between the V_3O_9 chains and is coordinated with ten oxygens. The present study demonstrates the applicability of hydrothermal method to the synthesis of new and/or metastable lanthanide vanadates. © 2000 Academic Press

INTRODUCTION

Lanthanide orthovanadates LnVO_4 are major compounds in the Ln_2O_3 – V_2O_5 systems, which have been well characterized in physical properties as well as in crystallographic properties. Kitayama and co-workers (1) made extensive studies of the phase diagrams for Ln_2O_3 – V_2O_3 – V_2O_5 systems and reported the existence of some lanthanide vanadates other than LnVO_4 , but their crystallographic details have remained unknown. The orthovanadate crystallizes in two types, namely, tetragonal zircon (ZrSiO_4) type (2) and monoclinic monazite (CePO_4) type (3). Generally the larger Ln^{3+} ion prefers the monazite type due to its higher oxygen coordination number of 9 as compared

to 8 of the zircon type. For this reason LnVO_4 crystallizes solely in the monazite type in an equilibrium state and other orthovanadates including Sc and Y crystallize in the zircon type (4). It is interesting to note that CeVO_4 locating in the boundary of zircon and monazite types exhibits three polymorphs of CeVO_4 -I (zircon type), -II (monazite-type), and -III (scheelite type) when the pressure is increased, where unit cell volumes decrease in this order, namely, 353.5 Å³ for CeVO_4 -I, 326.6 Å³ for CeVO_4 -II, and 316.0 Å³ for CeVO_4 -III (5). As exemplified in CeVO_4 , zircon-type LnVO_4 at ambient pressure could be transformed to metastable monazite-type LnVO_4 by pressurization because the latter is expected to be a higher-pressure phase. However, the inverse case of the transition from stable monazite to metastable zircon type seems to be improbable.

In order to obtain metastable phases, solution processes categorized in “soft chemistry” sometimes work well. Actually, the synthesis of the tetragonal LaVO_4 was first reported by Ropp and Carroll (6), who utilized the reaction $\text{La}^{3+} + \text{VO}^{2+} + \text{NH}_4\text{OH} + \text{Cl}^- + \text{H}_2\text{O}_2 \rightarrow \text{LaVO}_4 + \text{N}_2 + \text{H}_4\text{Cl} + \text{H}_2\text{O}$ and obtained a low-crystalline product. Later Escobar and Baran (7) used NH_4VO_3 solution to which $\text{La}(\text{NO}_3)_3$ was added followed by aging at 50 – 60°C and obtained tetragonal LaVO_4 for which the zircon type was suggested by powder X-ray diffractometry and IR spectroscopy. However, Chakoumakos *et al.* (4) recently claimed that they failed to synthesize zircon-type LaVO_4 by accurate duplications of the reported synthetic methods. So they could not include LaVO_4 in their study of the structure refinements of zircon-type LnVO_4 from neutron powder diffraction data. Therefore, it is required to develop a more reproducible synthetic method of zircon-type LaVO_4 that has hopefully high crystallinity.

Among various methods of soft chemistry, hydrothermal methods are useful to synthesize metastable or novel compounds in high crystallinity. The methods have been fruitful

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for vanadium oxide compounds in our studies (8). In the present study, hydrothermal methods have been successfully applied to the La-V-O system to produce zircon-type LaVO_4 and a new compound LaV_3O_9 in a single-crystalline form. Single-crystal structural characterization has been made on both compounds as well as the investigation of hydrothermal synthetic conditions.

EXPERIMENTAL PROCEDURES

Sample Preparation

Starting materials for the La-V-O hydrothermal system were LaCl_3 , $\text{La}_2(\text{SO}_4)_3$, and $\text{La}(\text{NO}_3)_3$ for La sources and V_2O_5 , $\text{VO}(\text{OH})_2$, and NaVO_3 for V sources. Mixed suspensions with various La/V molar ratios were prepared and sealed in Pyrex ampoules followed by hydrothermal treatments at 220–280°C for 24–48 h. Precipitates were filtered out and washed thoroughly with distilled water. Main products of the present system were white powders, colorless prismatic crystals, and yellow flat crystals. The white powders and colorless crystals were identified as monoclinic and/or tetragonal LaVO_4 by powder X-ray diffractometry. The yellow crystals were always obtained together with the white powders, which were easily removed by repeated sonication and decantation. However, powder X-ray diffractometry failed to identify the yellow crystal. An EDX analysis gave the molar ratio $\text{La}/\text{V} = \frac{1}{3}$ and a thermogravimetric analysis up to 500°C showed no weight change due to dehydration or redox reaction. Taking into account that the yellow color indicates a $\text{La}^{\text{III}}\text{-V}^{\text{V}}\text{-O}$ compound, the composition of the yellow crystal was determined as LaV_3O_9 .

Single-Crystal X-Ray Diffraction

Single-crystal X-ray diffraction studies were carried out on tetragonal LaVO_4 to confirm the zircon structure and on LaV_3O_9 to solve its unknown structure.

Crystals suitable for single-crystal X-ray diffractometry were selected for Weissenberg camera work. Crystals with dimensions of $0.20 \times 0.10 \times 0.05$ mm for LaVO_4 and $0.10 \times 0.05 \times 0.05$ mm for LaV_3O_9 were mounted on a Rigaku AFC-7R diffractometer with monochromatized $\text{MoK}\alpha$ radiation. The tetragonal system $I4_1/amd$ was confirmed for LaVO_4 with cell parameters $a = 7.4578(7)$ Å and $c = 6.5417(9)$ Å determined from 25 reflections of $28.3^\circ < 2\theta < 38.9^\circ$ and the monoclinic system $P2_1/m$ for LaV_3O_9 with $a = 4.949(2)$ Å, $b = 9.547(2)$ Å, $c = 7.411(2)$ Å, and $\beta = 100.76(2)^\circ$ from 25 reflections of $28.5^\circ < 2\theta < 29.7^\circ$. Data collections were made using the 2θ - ω scanning method up to $2\theta = 80^\circ$ with scan widths $\Delta\omega = (1.78 + 0.30 \tan \theta)^\circ$ for LaVO_4 and $(0.94 + 0.30 \tan \theta)^\circ$ for LaV_3O_9 , where three standard reflections were monitored every 150 data and no significant intensity fluctuations

TABLE 1
Experimental and Crystallographic Parameters of LaVO_4 and LaV_3O_9

	LaVO_4	LaV_3O_9
Space group	$I4_1/amd$	$P2_1/m$
a (Å)	7.4578(7)	4.929(2)
b (Å)	7.4578(7)	9.547(2)
c (Å)	6.5417(9)	7.411(2)
β (°)	90	100.76(2)
V (Å ³)	363.84(4)	344.0(2)
Z	4	2
D_c (g cm ⁻³)	4.634	4.206
μ (MoK α) (cm ⁻¹)	139.5	100.3
No. of reflections ($I > 0$)	357	2229
No. of reflections ($I > 3\sigma(I)$)	276	1868
No. of variables	12	68
R/R_w	0.020/0.025	0.035/0.042
$\Delta\rho_{\text{max/min}}$ (e/Å ³)	1.42/ - 0.90	1.84/ - 1.49

were detected for either crystal. No decay correction was thus applied. Empirical absorption corrections of the ψ scan method were applied resulting in the transmission factors 0.139–0.200 for LaVO_4 and 0.310–0.367 for LaV_3O_9 . The threshold for data to be used in the refinements was given as $I > 3\sigma(I)$. All the data processing and structure refinement calculations were performed by using *teXsan* for Windows (9). Experimental parameters are listed in Table 1.

It was first examined if the tetragonal LaVO_4 have the zircon-type structure or its modified one. The refinements using the crystallographic parameters of the zircon type successfully converged to $R = 0.020$ and $R_w = 0.025$, and no anomaly was detected. The tetragonal LaVO_4 is therefore confirmed to have the normal zircon-type structure. The structure of LaV_3O_9 was solved by the direct method provided by the *teXsan* for Windows and subsequent differential Fourier techniques. One La, two V, and six O atoms were located consistently, and the refinements converged to $R = 0.035$ and $R_w = 0.042$. Crystallographic data as well as experimental parameters are listed in Table 1 and atomic coordinates and equivalent temperature factors in Tables 2 and 3 for LaVO_4 and LaV_3O_9 , respectively (10).

TABLE 2
Atomic Coordinates and Equivalent Temperature Factors for Zircon-type LaVO_4

Atom	x	y	z	B_{eq} (Å ²)
La	0	$\frac{3}{4}$	$\frac{1}{8}$	0.560(3)
V	0	$\frac{1}{4}$	$\frac{3}{8}$	0.577(7)
O	0	0.4272(3)	0.2083(3)	0.95(3)

TABLE 3
Atomic Coordinates and Equivalent Temperature Factors
for LaV_3O_9

Atom	x	y	z	$B_{\text{eq}} (\text{\AA}^2)$
La	0.07592(5)	$\frac{1}{4}$	0.00207(3)	0.744(4)
V(1)	0.55770(9)	0.07224(5)	0.69782(6)	0.571(7)
V(2)	0.741457(14)	$\frac{1}{4}$	0.35534(9)	0.631(9)
O(1)	0.2178(5)	0.0087(3)	0.1440(3)	1.20(4)
O(2)	0.6188(6)	$\frac{1}{4}$	0.1295(4)	0.95(5)
O(3)	0.2866(5)	0.1108(3)	0.7835(3)	1.21(4)
O(4)	0.6159(4)	0.0910(3)	0.4410(3)	0.93(3)
O(5)	0.7259(6)	$\frac{1}{4}$	0.7221(4)	0.81(5)
O(6)	0.0733(7)	$\frac{1}{4}$	0.3598(5)	1.24(6)

RESULTS AND DISCUSSION

Description of Structures

The tetragonal LaVO_4 has been confirmed to be a member of zircon-type lanthanide orthovanadate, which has the largest cell dimensions. As depicted in Fig. 1, zircon-type LaVO_4 consists of isolated VO_4 tetrahedra and La atoms. The VO_4 tetrahedron shows a regular shape with a constant V–O bond distance of 1.713(3) \AA and a O–V–O bond angle of 113.9(1) $^\circ$. The La atoms are coordinated by eight oxygens, as depicted in Fig. 2, forming a LaO_8 dodecahedron in which the La atom bonds to four vertices of VO_4 with La–O = 2.468(3) \AA and two edges of VO_4 with La–O = 2.550(3) \AA . Chakoumakos *et al.* (4) investigated structures of zircon-type lanthanide orthovanadate except LaVO_4 and

derived empirical relationships between crystal parameters and lanthanide ionic radii. By applying their equations to zircon-type LaVO_4 , the following results are obtained: $a = 7.4308 \text{ \AA}$ and $c = 6.5268 \text{ \AA}$ for cell parameters and $x = 0.4269$ and $z = 0.2072$ for oxygen positional coordinates, which are compared with our experimental values of $a = 7.4578(7) \text{ \AA}$, $c = 6.5417(9) \text{ \AA}$, $x = 0.4272(3)$, and $z = 0.2083(3)$. Their cell parameters are somewhat underestimated, while their oxygen positional coordinates do give adequate estimates.

The monoclinic LaV_3O_9 is a new compound, and no LnV_3O_9 phase has been found for other Ln elements (1). The structure is depicted in Fig. 3, which can be denoted as a chain-type V–O framework structure consisting of VO_4 tetrahedra and distorted VO_5 trigonal bipyramids for which V–O bond distances and O–V–O bond angles are listed in Table 4. The V–O chain is constructed in the following manner. Two VO_5 trigonal bipyramids form a $\text{VO}_5\text{--VO}_5$ unit by sharing edges, and the units are linked by sharing their vertices to make up a $\text{VO}_5\text{--VO}_5$ zigzag chain along

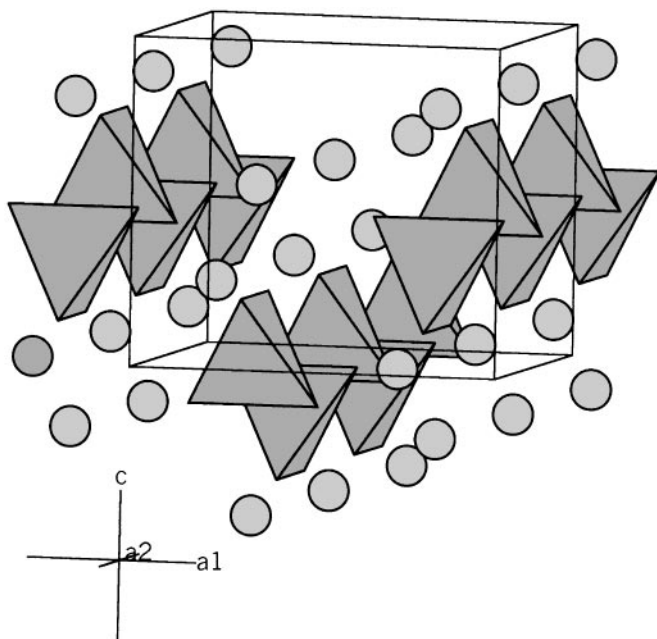


FIG. 1. Crystal structure of the zircon-type LaVO_4 . Tetrahedra and circles denote the VO_4 tetrahedra and the La atoms, respectively.

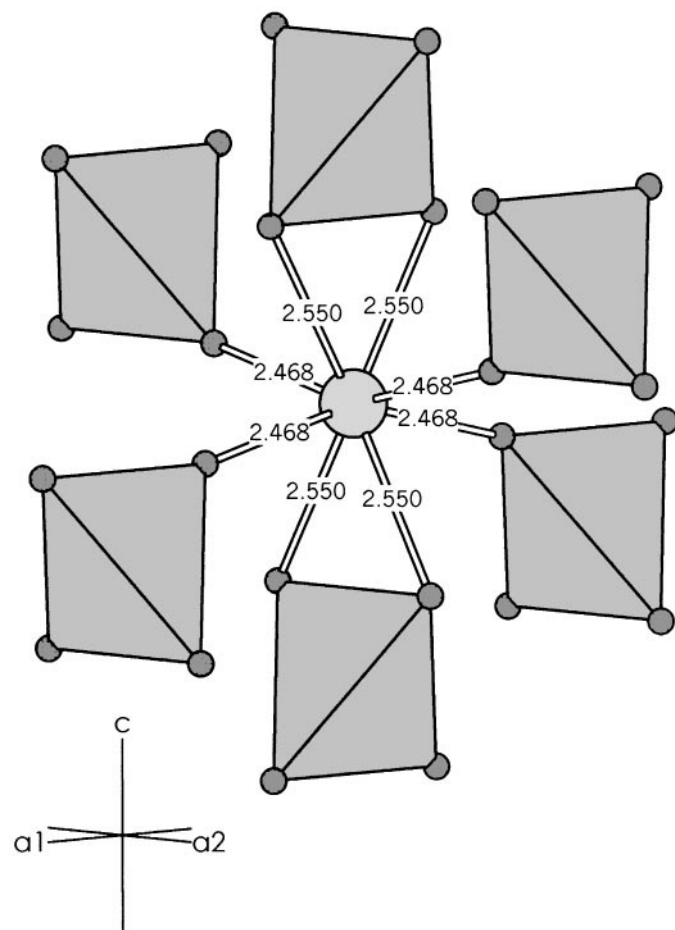


FIG. 2. Oxygen coordination around the La atom in the zircon-type LaVO_4 . The La and O atoms are denoted by large and small circles, respectively.

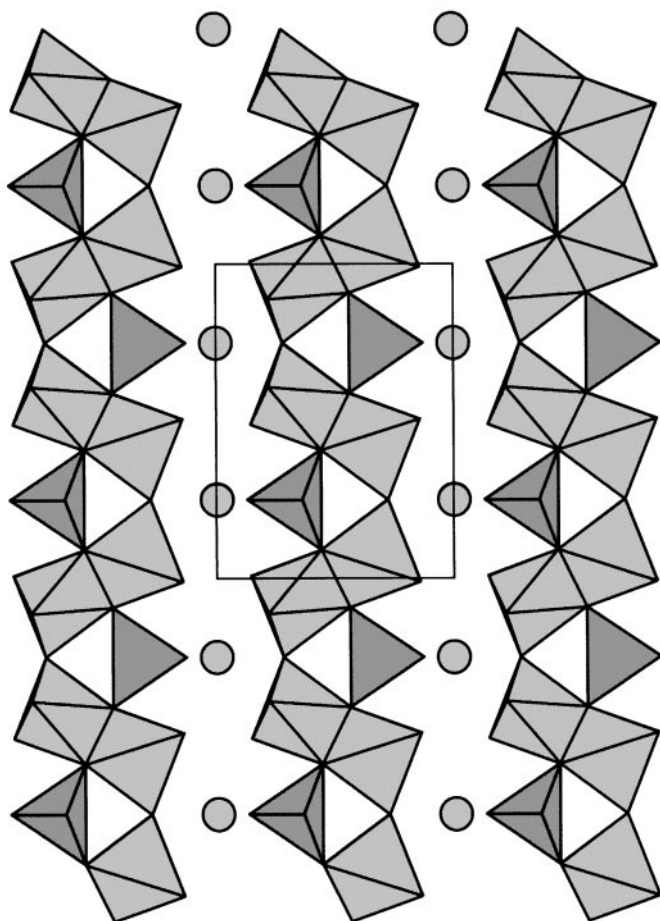


FIG. 3. Crystal structure of LaV_3O_9 viewed along $[010]$. The V_3O_9 chain is depicted by the VO_4 tetrahedral and VO_5 trigonal-bipyramidal representation, and the La atom is denoted by a shaded circle.

$[010]$. The framework of the zigzag VO_5 - VO_5 chain is stabilized by placing VO_4 tetrahedra to connect neighboring VO_5 - VO_5 units by sharing vertices of shared VO_5 - VO_5 edges. The VO_4 tetrahedra in the zigzag chain point toward $[100]$ and $[-100]$ alternately. The V_3O_9 chain is thus constructed. The LaV_3O_9 structure is classified into a chain-type structure which is uncommon in lanthanide vanadates. The La atom is placed in a slightly zigzag row along $[010]$. As depicted in Fig. 4, it is coordinated by ten oxygens of neighboring four V_3O_9 chains to form a LaO_{10} polyhedron for which La-O bond distances are listed in Table 5. The 10-coordination of La^{3+} ion is higher than the 9-coordination in the monazite-type LaVO_4 , and it would be the highest coordination in lanthanum vanadates except for the perovskite-type LaVO_3 .

Hydrothermal Synthesis of Zircon-Type LaVO_4 and LaV_3O_9

As described in the preceding section, the thermodynamically equilibrium phase of LaVO_4 in the monazite

TABLE 4
V-O Bond Distances (Å) and O-V-O Bond Angles (Deg) in V-O Polyhedra for LaV_3O_9

V(1)O ₅ trigonal bipyramid					
V(1)-O(1) ⁱ	1.649(3)	V(1)-O(3)	1.630(3)	V(1)-O(4)	1.986(3)
V(1)-O(4) ⁱ	1.974(3)	V(1)-O(5)	1.884(2)		
O(1) ⁱ -V(1)-O(3)	108.9(2)	O(1) ⁱ -V(1)-O(4)	121.6(2)		
O(1) ⁱ -V(1)-O(4) ⁱ	99.8(1)	O(1) ⁱ -V(1)-O(5)	97.3(2)		
O(3)-V(1)-O(4)	129.1(2)	O(4)-V(1)-O(4) ⁱ	94.1(1)		
O(3)-V(1)-O(5)	98.1(2)	O(4)-V(1)-O(4) ⁱ	72.5(1)		
O(4)-V(1)-O(5)	82.5(2)	O(4) ⁱ -V(1)-O(5)	154.5(2)		
V(2)O ₄ tetrahedron					
V(2)-O(2)	1.671(4)	V(2)-O(4)	1.800(3)	V(2)-O(4) ⁱⁱ	1.800(3)
V(1)-O(6) ⁱⁱⁱ	1.636(4)				
O(2)-V(2)-O(4)	105.6(1)	O(2)-V(2)-O(4) ⁱⁱ	105.6(1)		
O(2)-V(2)-O(6) ⁱⁱⁱ	101.3(2)	O(4)-V(2)-O(4) ⁱⁱ	114.9(2)		
O(4)-V(2)-O(6) ⁱⁱⁱ	113.9(1)	O(4) ⁱⁱ -V(2)-O(6) ⁱⁱⁱ	113.9(1)		

Note. Symmetry codes: (i) $1-x, -y, 1-z$; (ii) $x, \frac{1}{2}-y, z$; (iii) $1+x, y, z$.

phase, and the synthetic methods of the zircon-type LaVO_4 so far reported (6, 7) have recently been revealed not to work (4). Here we have explored a reproducible way to the zircon-type LaVO_4 , where the key factors were found to be starting materials. The starting materials are already listed in the experimental section and the main products yielded from the combination of La and V sources are tabulated in Table 6 where the concentration of La^{3+} was fixed to 0.1

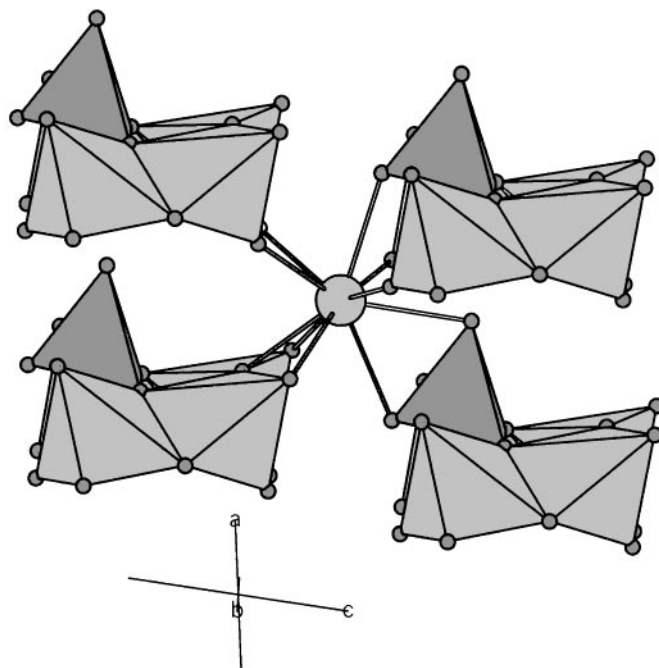


FIG. 4. Oxygen coordination around the La atom in LaV_3O_9 , demonstrating that the La atom is surrounded by four V_3O_9 chains. The La and O atoms are denoted by large and small circles, respectively.

TABLE 5
La–O Bond Distances (Å) in LaV₃O₉

La–O(1) ^{i,ii}	2.575(3)	La–O(1) ^{iii,iv}	2.966(3)	La–O(2) ⁱ	2.676(4)
La–O(2) ^v	2.609(4)	La–O(3) ^{vi,vii}	2.472(3)	La–O(5) ^{viii}	2.442(4)
La–O(6) ⁱ	2.653(5)				

Note. Symmetry codes: (i) x, y, z ; (ii) $x, \frac{1}{2} - y, z$; (iii) $-x, \frac{1}{2} + y, -z$; (iv) $-x, -y, -z$; (v) $x - 1, y, z$; (vi) $x, y, z - 1$; (vii) $x, \frac{1}{2} - y, z - 1$; (viii) $x - 1, y, z - 1$.

M and the La/V molar ratios were varied in a range of 1/6 to 6/1. The products of the present hydrothermal systems are all La–V^V–O compound and the attempts to produce V^{IV/V} mixed-valence lanthanum vanadates were unsuccessful: the main products are LaVO₄ of both zircon and monazite types and LaV₃O₉. Reaction temperatures were not crucial as long as they are above ca. 220°C.

It is said that regardless of V sources La(NO₃)₃ always produced monazite-type LaVO₄. Other La sources of LaCl₃ and La₂(SO₄)₃ produced mainly zircon-type LaVO₄, but a monazite-type one was included in a small amount. Comparing the two La sources, we found that La₂(SO₄)₃ worked better than LaCl₃ in producing zircon-type LaVO₄. It should be noted that the VO(OH)₂–La₂(SO₄)₃ system with higher La/V ratios produced monophasic zircon-type LaVO₄. In this case no oxidizing agent was required. Consequently two polymorphs of LaVO₄ can be synthesized separately using the hydrothermal methods by choosing appropriate La and V sources. For example, the failure of Chakoumakos *et al.* (4) in synthesizing zircon-type LaVO₄ following the method of Escobar and Baran (7) would be due to using La(NO₃)₃.

The new compound LaV₃O₉ was formed for the La sources of LaCl₃ and La₂(SO₄)₃ and the V sources of V₂O₅ and NaVO₃ with relatively lower La/V ratios. The product of LaV₃O₉ always appeared as yellow prismatic crystals. It

TABLE 6
Hydrothermal Products in the La–V–O System for La and V Source Combinations

V source	La source		
	LaCl ₃	La ₂ (SO ₄) ₃	La(NO ₃) ₃
V ₂ O ₅	LaVO ₄ (zircon > monazite) LaV ₃ O ₉	LaVO ₄ (zircon) LaV ₃ O ₉	LaVO ₄ (monazite)
VO(OH) ₂	LaVO ₄ (zircon > monazite)	LaVO ₄ (zircon)	LaVO ₄ (monazite)
NaVO ₃	LaVO ₄ (zircon = monazite) LaV ₃ O ₉	LaVO ₄ (zircon) LaV ₃ O ₉ NaLa(SO ₄) ₂ · H ₂ O	LaVO ₄ (monazite)

is noted that the La source of La(NO₃)₃ and the V source of VO(OH)₂ never produced LaV₃O₉ crystals.

Both zircon-type LaVO₄ and LaV₃O₉ are in a metastable state, and thus their thermal stability was examined using DTA and thermal annealing. DTA measurements were carried out up to 800°C at a heating rate of 5°C min⁻¹. The zircon-type LaVO₄ showed no appreciable exothermic peak even though the phase was changed to the monazite. The transition point from zircon to monazite is expected below 600°C, since thermal annealing at 500°C for 2 h showed no change while that at 600°C for 2 h formed the monazite phase. The thermal stability is a little higher than that Escobar and Baran (7) who reported that the phase change occurred by annealing at 500°C for 1 h. LaV₃O₉ likewise showed no sign of the phase change in a DTA curve although the melting behavior of V₂O₅ was clearly seen, indicating LaV₃O₉ was gradually decomposed into LaVO₄ and V₂O₅ below 670°C. The thermal stability of LaV₃O₉ should be up to 500°C at best as examined by thermal annealing.

CONCLUSION

Hydrothermal methods were successfully applied to the synthesis of lanthanum vanadate metastable compounds, namely, zircon-type LaVO₄ and a new phase LaV₃O₉ for which other methods like solid-state and mild-solution processes do not work well. For producing zircon-type LaVO₄, the La source of La₂(SO₄)₃ or the SO₄²⁻ environment was found to be the most effective while that of La(NO₃)₃ or NO₃⁻ environment to have no effect. The synthetic conditions of LaV₃O₉ were similar to those of zircon-type LaVO₄ except that the V sources of V^{IV} compounds never produced LaV₃O₉.

The zircon-type structure of LaVO₄ has been confirmed by single-crystal X-ray diffractometry. The structure of LaV₃O₉ has also been determined using a single crystal, which has turned out a chain-type structure being rare in lanthanide vanadate compounds. The V₃O₉ chain consists of edge-sharing VO₅ trigonal-bipyramidal units and VO₄ tetrahedra connecting to the units by sharing vertices.

An attempt to hydrothermally synthesize metastable or new lanthanide vanadates other than La is in progress and will be reported elsewhere.

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10. Further details of the crystal structure determination can be ordered from FACHIN Formationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, under the depository numbers CSD-411083 for LaVO_4 and CSD-411084 for LaV_3O_9 .