

Dimorphism in Triple Orthovanadates $M^{II}LaTh(VO_4)_3$ ($M^{II} = Sr$ or Pb)

MAHADEO A. NABAR* AND BAL G. MHATRE

Department of Chemistry, University of Bombay, Vidyanagari, Santacruz (East), Bombay, 400 098, India

Received December 17, 1981; in revised form April 16, 1982

Triple orthovanadates, $SrLaTh(VO_4)_3$ and $PbLaTh(VO_4)_3$ are found to be dimorphic, the crystalline form depending upon the firing temperature. The low-temperature form has zircon structure and the corresponding high-temperature form exhibits its well-known monoclinic modification. The X-ray powder diffractograms and infrared spectra are recorded and discussed in comparison with those of structurally related compounds.

Introduction

Carron *et al.* (1) have compiled the work on rare earth oxo-salts, $LnXO_4$ ($X = P^V, As^V, V^V$), and attributed the structural change from monazite (the monoclinic huttonite-type structure) to xenotime (the tetragonal zircon-type structure) in these series to the well-known lanthanide contraction. While studying the effect of high pressure at temperatures up to 873K, on the rare earth *ortho*-arsenates and -vanadates, Stubican and Roy (2) achieved the reconstructive transformation from xenotime \rightleftharpoons scheelite structure in the case of a majority of arsenates (Sm-Lu) and vanadates (Pr-Lu), whereas monazite \rightleftharpoons scheelite transformation was observed in the case of $PrAsO_4$ and $NdAsO_4$. It would be interesting to mention here that the above authors could not achieve xenotime to monazite transformation for any of the rare earth

orthosalts. Against this background, Ropp and Carroll (3) observed that the crystalline form of $LaVO_4$ depends on the mode of preparation; the $LaVO_4$ prepared by solid-state reaction gives monoclinic form, whereas the precipitation of $LaVO_4$ from solution yields tetragonal form, which in turn gets converted to its monoclinic modification on heating above 573K.

In the case of orthovanadates of the formula $M_{0.5}^{II}Th_{0.5}VO_4$, Schwarz (4) has observed that the substitution of M^{II} by Cd, Ca, or Sr gives zircon structure, while the Pb^{II} -substituted compound exhibits polymorphism, giving rise to three crystalline forms—scheelite, zircon, and huttonite—with increase in temperature. Pages and Freundlich (5) identified the above three structural types in the double *ortho*-arsenates $M^I M_2^{IV}(AsO_4)_3$ and -vanadates $M^I M_2^{IV}(VO_4)_3$ and $M^{II} M^{IV}(VO_4)_2$ ($M^I = Li, Na, Ag$; $M^{II} = Cd, Ca, Pb$; $M^{IV} = Th, Np, Pu$), the structural stability being dependent on the ionic radii of the substituted cations.

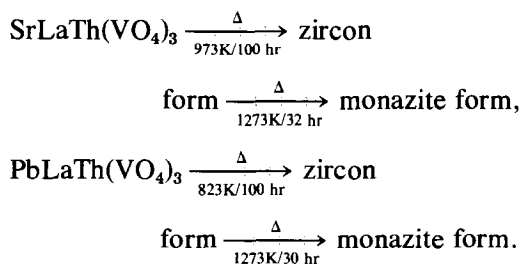
The study on triple *ortho*-vanadates,

* To whom all correspondence should be addressed.

$M^{II}\text{LaTh}(\text{VO}_4)_3$, carried out in this laboratory showed that $\text{CdLaTh}(\text{VO}_4)_3$ (6) and $\text{CaLaTh}(\text{VO}_4)_3$ (7) crystallize with zircon structure, whereas $\text{BaLaTh}(\text{VO}_4)_3$ (7) exhibits monazite structure. Therefore, it seemed interesting to investigate the effect of temperature and that of the compensatory divalent cations having ionic radii between those of calcium and barium on the structural behavior of such triple *ortho*-vanadates.

Experimental

The triple *ortho*-vanadates were prepared by initially mixing the stoichiometric quantities of AnalaR-grade oxides, carbonates, or nitrates of the respective metals with ammonium *meta*-vanadate in aqueous medium. The suspended precipitates so obtained were evaporated to dryness, well mixed, and heated at 573K for 6 hr. Subsequently, the residues were sintered for 30–100 hr at temperatures suitably selected (monitoring the crystallinity by scanning the X-ray powder patterns of the samples) in the form of well-pressed cylindrical pellets. Repeated cycles of grinding, pelleting, and heating were necessary to obtain homogeneous single-phase compounds free of unreacted material. The final sintering temperatures and time for obtaining the two different structural forms of $\text{SrLaTh}(\text{VO}_4)_3$ and $\text{PbLaTh}(\text{VO}_4)_3$ are



The X-ray powder patterns were obtained on a Philips X-ray diffractometer PH 1009/30/NRD 1023 using nickel-filtered

$\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The infrared spectra were recorded in the range 4000–200 cm^{-1} on a Beckman IR 4250 spectrophotometer, using conventional CsBr pressed-disk technique.

Results and Discussion

Crystal Structure

The X-ray powder patterns reveal that the low-temperature (LT) form of $M^{II}\text{LaTh}(\text{VO}_4)_3$ ($M^{II} = \text{Sr}$ or Pb) possesses zircon structure similar to that exhibited by rare earth *ortho*-vanadates (8, 9). X-Ray patterns of the high-temperature (HT) modifications, on the other hand, manifest the adoption of monazite structure (10). In compliance with the above observations, the LT forms were indexed on a tetragonal unit cell with space group $I4_1/amd$ and the corresponding HT dimorphs were indexed on a monoclinic unit cell with space group $P2_1/m$. The least-squares refined lattice dimensions are gathered in Table I, and the complete indexed powder diffraction data are given in Tables II and III.

Infrared Spectra

It must be pointed out that the infrared spectra of both the tetragonal and monoclinic forms have similar overall appearance and hence are not sufficient to differentiate both modifications as observed in the cases of LaVO_4 (9, 10) and PrCrO_4 (11). On the other hand, a detailed scrutiny of the spectra reproduced in Fig. 1 reveals that the VO_4 ions present in both forms of $\text{PbLaTh}(\text{VO}_4)_3$ are subjected to different types of symmetry lowering and/or correlation field effects. The aforementioned observation is in acquiescence with Tarte's remarks that, if one considers a series of compounds, not isomorphous but containing the same complex anion, the high-frequency absorption region remains the same, but the look of the spectrum, i.e., the

TABLE I
CELL DIMENSIONS OF TETRAGONAL AND MONOCLINIC VARIETIES OF SrLaTh(VO₄)₃ AND PbLaTh(VO₄)₃

Structural form	Compound	<i>a</i> (pm)	<i>b</i> (pm)	<i>c</i> (pm)	β (°)	10 ⁶ V (pm) ³	Z	<i>D</i> _{calcd} (mg m ⁻³)	<i>D</i> _{obs} (mg m ⁻³)
Tetragonal	SrLaTh(VO ₄) ₃	738.4 ± 0.3	—	651.9 ± 0.3	—	355	4	5.00	4.98
	PbLaTh(VO ₄) ₃	739.7 ± 0.3	—	654.2 ± 0.4	—	358	4	5.71	5.68
Monoclinic	SrLaTh(VO ₄) ₃	698.6 ± 0.4	722.7 ± 0.8	670.9 ± 0.5	105.20 ± 0.06	327	4	5.44	5.40
	PbLaTh(VO ₄) ₃	699.7 ± 0.5	724.7 ± 0.8	672.8 ± 0.6	105.05 ± 0.06	330	4	6.20	6.19

number, the intensity, and the position of the bands is modified (12).

The simplest interpretation of the infrared spectra of the LT form of *M*^{II}LaTh(VO₄)₃ (where *M*^{II} = Sr or Pb) compounds is in conformity with *D*_{2d} site symmetry for VO₄³⁻ ions, associated with zircon structure (9, 13–15). The isolated *T*_d point group of

the VO₄³⁻ ions, under *D*_{2d} site symmetry, gives four infrared active and seven Raman active vibrations:

$$\nu_1(A_1) \rightarrow A_1(R);$$

$$\nu_2(E) \rightarrow A_1(R) + B_1(R);$$

$$\nu_3, \nu_4(F_2) \rightarrow B_2(ir, R) + E(ir, R).$$

The number of bands observed in the stretching region is, however, more than that expected on the basis of site group approximation. The cause of this enrichment in the number of bands could be either factor group splitting and/or some asymmetry in the VO₄ ions in these lattices due to differences in the environment, polarizing powers, and charges of the cations present in the *M*^{II}LaTh(VO₄)₃ unit cells. In the bending region, the bands observed around 430 and 360 cm⁻¹ are attributable to two split components of triply degenerate ν_4 mode (Table IV).

The spectra of the HT forms of *M*^{II}LaTh(VO₄)₃ are almost exactly those to be expected on the basis of monazite structure where the VO₄³⁻ ions occupy *C*₁ sites (10, 13, 15). Under this site symmetry, all nine modes of vibrations of vanadate group are both infrared and Raman active as

$$\nu_1(A_1) \rightarrow A; \nu_2(E) \rightarrow 2A;$$

$$\nu_3, \nu_4(F_2) \rightarrow 3A.$$

TABLE II
X-RAY POWDER DIFFRACTION DATA OF
TETRAGONAL FORMS OF *M*^{II}LaTh(VO₄)₃ (*M*^{II} = Sr
OR Pb)

<i>h k l</i>	SrLaTh(VO ₄) ₃			PbLaTh(VO ₄) ₃		
	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>I</i> / <i>I</i> ₀	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>I</i> / <i>I</i> ₀
1 0 1	488	489	24	488	490	44
2 0 0	369	369	100	369	370	100
2 1 1	295	295	11	295	295	17
1 1 2	277	276	53	277	277	67
2 2 0	261	261	10	261	262	18
3 0 1	230	230	13	231	231	14
1 0 3	209	208	8	209	209	8
3 2 1	195.5	195.4	9	196.0	195.8	11
3 1 2	190.0	189.8	35	190.4	190.3	40
4 0 0	184.7	184.6	9	185.0	184.9	11
2 1 3	181.6	181.5	4	182.2	182.1	4
4 1 1	—	172.7	—	173.0	173.0	4
4 2 0	165.2	165.1	7	165.6	165.4	8
3 0 3	162.8	162.9	5	163.5	163.4	5
3 3 2	153.5	153.5	8	154.0	153.9	9
2 0 4	149.1	149.1	7	149.7	149.6	9
5 0 1	—	144.0	—	144.4	144.3	4

TABLE III
X-RAY POWDER DIFFRACTION DATA FOR
MONOCLINIC MODIFICATIONS OF $M^{II}LaTh(VO_4)_3$
($M^{II} = Sr$ OR Pb)

$h k l$	SrLaTh(VO_4) ₃			PbLaTh(VO_4) ₃		
	d_{obs}	d_{calc}	I/I_0	d_{obs}	d_{calc}	I/I_0
1 0 $\bar{1}$	542	543	8	542	544	18
0 1 1	482	482	13	483	484	22
1 1 $\bar{1}$	433	434	25	434	435	22
1 0 1	415	416	13	417	417	7
1 1 1	361	361	25	362	362	24
2 0 0	337	337	70	338	338	93
1 2 0	318	319	100	319	319	100
2 1 0	306	306	15	306	306	16
0 1 2	296	296	60	297	297	46
2 0 $\bar{2}$	272	272	18	272	272	20
2 1 $\bar{2}$	255	254	18	255	255	18
1 1 2	250	250	8	251	251	7
2 2 0	247	247	5	247	247	5
1 2 $\bar{2}$	—	243	—	243	243	4
1 3 0	226	227	8	227	228	15
1 0 $\bar{3}$	224	223	10	224	224	11
3 1 $\bar{1}$	221	221	10	221	221	13
2 2 1	217	217	8	218	218	7
2 1 2	200	199.9	20	201	201	35
3 0 1	196.6	197.0	10	197.5	197.6	9
1 3 $\bar{2}$	194.2	194.0	18	194.8	194.5	13
1 0 3	191.3	191.6	13	191.6	192.3	15
1 1 3	—	185.2	—	186.3	185.8	5
3 2 $\bar{2}$	183.4	183.1	13	183.9	183.5	9
3 0 $\bar{3}$	180.9	181.1	10	181.3	181.4	11
1 3 2	179.0	178.6	18	179.6	179.1	13
4 0 $\bar{1}$	174.7	174.6	8	175.0	174.9	7
4 0 0	168.6	168.6	8	169.1	168.9	13
4 1 0	164.4	164.2	10	164.7	164.5	7
0 0 4	161.9	161.9	5	—	162.4	—
2 1 3	159.6	159.5	8	160.0	160.0	7

The general appearance of the spectra are in good agreement with the low site symmetry of the *ortho*-vanadate ions, though the degenerate bands are not fully resolved. The high-frequency region (1000–600 cm^{-1}) corresponding to ν_1 and ν_3 stretching vibrations of VO_4^{3-} ions is characterized by a very broad absorption with a few well-defined bands (Table V). The peculiar shape of absorption in the stretching region could be ascribed to crystal structure, since simi-

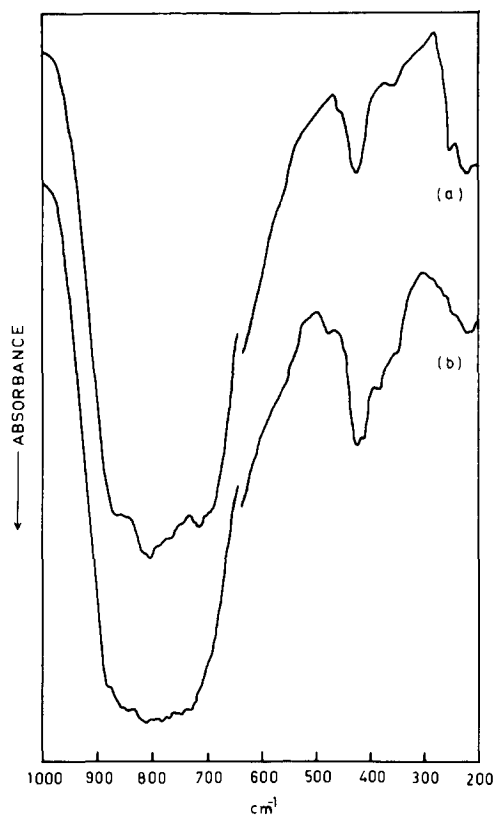


FIG. 1. Infrared spectra of $PbLaTh(VO_4)_3$; (a) tetragonal form, (b) monoclinic form.

lar behavior has been observed for the isostructural $LaVO_4$ (10). No attempt was made to assign the observed bands to spe-

TABLE IV
FREQUENCIES OF THE INFRARED ACTIVE
VIBRATIONS FOR TETRAGONAL $SrLaTh(VO_4)_3$ AND
 $PbLaTh(VO_4)_3$ IN cm^{-1} AT 25°C

SrLaTh(VO_4) ₃	PbLaTh(VO_4) ₃	Assignments
880 (sh)	869 (sh)	ν_3
827 (vs)		
778 (s)	802 (vs)	
727 (s)	766 (sh)	
	714 (s)	ν_4
433 (m)	427 (w)	
375 (w)	356 (vw)	

Note. s: strong; vs: very strong; m: medium; w: weak; vw: very weak; sh: shoulder.

TABLE V
FREQUENCIES OF THE INFRARED ACTIVE
VIBRATIONS FOR MONOCLINIC SrLaTh(VO₄)₃ AND
PbLaTh(VO₄)₃ IN cm⁻¹ AT 25°C

SrLaTh(VO ₄) ₃	PbLaTh(VO ₄) ₃	Assignments
894 (sh)		} ν_1/ν_3
866 (s)	876 (sh)	
823 (s)	838 (sh)	
791 (s)	808 (s)	
772 (sh)	778 (s)	
756 (sh)	765 (sh)	
735 (sh)	748 (sh)	
723 (s)	729 (sh)	
479 (sh)	477 (vw)	} ν_2/ν_4
436 (sh)		
422 (m)	423 (m)	
400 (sh)	409 (sh)	
383 (sh)	381 (w)	
370 (sh)		
351 (sh)	348 (sh)	

Note. s: strong; m: medium; w: weak; vw: very weak; sh: shoulder.

cific modes in this region. In the bending region also, the spectra are indicative of low-symmetry sites, though ν_2 and ν_4 are not completely resolved. Due to the proximity in the symmetric and asymmetric O–V–O bending modes of VO₄³⁻ ions, no further attributions could be made.

Conclusions

The X-ray diffraction and infrared spectral studies clearly indicate the dimorphism in SrLaTh(VO₄)₃ and PbLaTh(VO₄)₃ compounds. It is interesting to note that the average ionic radii of the cations in LaVO₄ (3), PbTh(VO₄)₂ (4), and the compounds considered under the present investigation,

exhibiting zircon to monazite phase transformation, lie between 106 and 110 pm.

Acknowledgments

The authors are thankful to Tata Institute of Fundamental Research for providing the facility for X-ray diffractograms and the Department of Computer Science of the University for the computation work. One of the authors (B.G.M.) acknowledges financial assistance by the University of Bombay.

References

1. M. K. CARRON, M. E. MROSE, AND K. J. MURATA, *Amer. Miner.* **43**, 985 (1958).
2. V. S. STUBICAN AND R. ROY, *Z. Krist.* **119**, 90 (1963).
3. R. C. ROPP AND B. CARROLL, *J. Inorg. Nucl. Chem.* **35**, 1153 (1973).
4. H. SCHWARZ, *Z. Anorg. Allg. Chem.* **334**, 261 (1965).
5. M. PAGES AND W. FREUNDLICH, "Plutonium and Other Actinides: Proceedings, 1975" (H. Blank and R. Lindner, Eds.), pp. 205–207, North-Holland, Amsterdam (1976).
6. M. A. NABAR, B. G. MHATRE, AND A. P. VASAIKAR, *J. Appl. Crystallogr.* **14**, 469 (1981).
7. M. A. NABAR, B. G. MHATRE, AND A. P. VASAIKAR, Unpublished results.
8. H. SCHWARZ, *Z. Anorg. Allg. Chem.* **323**, 50 (1963).
9. M. E. ESCOBAR AND E. J. BARAN, *Z. Anorg. Allg. Chem.* **441**, 273 (1978).
10. E. J. BARAN AND P. J. AYMONINO, *Z. Anorg. Allg. Chem.* **383**, 220 (1971).
11. S. G. MANCA AND E. J. BARAN, *J. Phys. Chem. Solids* **42**, 923 (1981).
12. P. TARTE, *Mem. Acad. Roy. Med. Belg.* **35**, 4a and 4b, 211 (1965).
13. R. G. BROWN AND S. D. ROSS, *Spectrochim. Acta Part A* **26**, 955 (1970).
14. E. J. BARAN AND P. J. AYMONINO, *Z. Anorg. Allg. Chem.* **383**, 226 (1971).
15. A. HAZEL AND S. D. ROSS, *Spectrochim. Acta* **22**, 1949 (1966).