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Studies on triple orthovanadates
VIII. Synthesis and spectrostructural characterization of triple orthovanadates $BaLnTh(VO_4)_3$ (Ln=La or Pr) and $BaLnCe(VO_4)_3$ (Ln=La, Pr, Nd or Sm)[☆]

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Abstract

To study the effect of substitution at the tetravalent ion, some barium lanthanide containing triple orthovanadates have been synthesised and structurally examined. The X-ray diffraction and the infrared spectroscopic data are analysed and interpretations are reported. It is observed that thorium containing compounds crystallise with a monoclinic monazite structure while those containing cerium are tetragonal superstructured zircon. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Lanthanon containing double and triple orthosalts obtained by charge compensation substitution reactions from rare earth salts, $LnXO_4$ (where, X=P, As, Cr(V) or V) are known to crystallize either in monazite or zircon structures [1–6].

The studies of lanthanon containing triple orthovanadates carried out in this laboratory agreed with the reported quantitative A:B relationship between the oxygen–central atom distances and the average of the six-fold cationic radii and the adopted structure, the value 1.86 being seemingly the highest limiting value for the monazite structure to occur [6,7]. Accordingly, $CaLaTh(VO_4)_3$ and $BaLaTh(VO_4)_3$ crystallize in zircon and monazite structures, respectively, and the corresponding strontium and lead containing triple orthovanadates exhibit dimorphism [8–11]. The present paper, which forms an extension of this comprehensive study, is directed to asses the effects of the substitution of rare-earth ion and of cerium substitution at tetravalent site (independently) on the structural stability by studying the triple orthovanadates, $BaLnTh(VO_4)_3$ (where Ln=La or Pr) and $BaLnCe(VO_4)_3$ (where Ln=La, Pr Nd or Sm).

2. Experimental

The triple orthovanadates under study were prepared using standard pyrotechniques, following mechano-chemical treatment. The synthesis consisted of treating stoichiometric quantities of the desired metal nitrates with ammonium metavanadate in aqueous media and thorough mixing for 1 h. The well-mixed solutions were evaporated to dryness, ground and heated initially at 623 K for 20 h and then air fired for 50–100 h in the form of well-pressed discs at temperatures suitably selected in the range of 823–1423 K with repeated cycles of grinding, pelleting and sintering, to obtain a single phase product with the degree of crystallinity monitored by X-ray diffraction (XRD). The X-ray powder patterns were obtained on a Phillips X-ray diffractometer PW/1009/30/NRD 1023, using nickel-filtered copper radiation. The infrared spectra were also recorded in the range 4000–200 cm^{-1}, using CsBr as a matrix, on a Beckman IR-4250 dual beam spectrophotometer.

3. Results

The XRD patterns of the compounds $BaLnTh(VO_4)_3$ where Ln=La or Pr, show them to be isomorphous with monazite structure as expected from the A:B ratio. These

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Table 1
Crystallographic contents for triple orthovanadates

Structural form	Compound	a (pm)	b (pm)	c (pm)	β (°)	$V \times 10^6$ (pm^3)	$D_{calcd.}$ ($mg\ m^{-3}$)	$D_{obsd.}$ ($mg\ m^{-3}$)
Monoclinic (monazite structure)	$BaLaTh(VO_4)_3$	707.0 ±0.5	732.3 ±0.8	681.0 ±0.6	104.96 ±0.07	340.8	5.54	5.52
	$BaPrTh(VO_4)_3$	706.6 ±0.5	731.5 ±0.8	680.1 ±0.7	104.94 ±0.08	339.7	5.57	5.54
Tetragonal (zircon super-structure)	$BaLaCe(VO_4)_3$	2221±3		645±2		3184.6	4.76	4.75
	$BaPrCe(VO_4)_3$	2207±1		643±0		3131.3	4.86	4.84
	$BaNdCe(VO_4)_3$	2204±1		641±1		3114.6	4.90	4.88
	$BaSmCe(VO_4)_3$	2198±3		640±0		3090.2	4.98	4.95

compounds thus are indexed on the monoclinic unit cell having space group $P2_1/n$ (C^5_{2h}). The neodymium or samarium containing thorium triple orthovanadates indicate the presence of minor impurity. Repeated attempts to obtain pure single phase compounds by varying the sintering period and/or temperature in these cases remained unsuccessful.

The XRD patterns of the triple orthovanadates $BaLnCe(VO_4)_3$, Ln=La, Pr, Nd or Sm, were indexed on a tetragonal zircon super-structure, with a space group $I4_1/amd$ by tripling the unit cell a axis. Freundlich et al. [12,13] have reported similar observations for $NaNp_2(AsO_4)_3$ and $LiTh_2(V_{0.25}As_{0.75}O_4)_3$. Furthermore, $Ca_{0.7}Ba_{0.3}LaTh(VO_4)_3$ obtained at 1473 K also has a similar zircon super-structure [11]. The least squares refined lattice dimensions of all compounds are catalogued in Table 1, and the complete indexed data of the representative compounds namely $BaLaTh(VO_4)_3$ and $BaPrCe(VO_4)_3$ are given in Tables 2 and 3, respectively.

The frequencies of the infrared vibrational spectra of these monazite and zircon super-structure modifications are catalogued in Tables 4 and 5. The assignments of the various bands are made by the comparison with the existing reports.

The infrared spectra of the monoclinic forms $BaLnTh(VO_4)_3$, suggest that the VO_4^{3-} ions occupy C_1 sites [14–16]. Under this site symmetry all nine modes of vibrations of vanadate group are infrared active. The spectral details are in good agreement with low site symmetry of the ortho-vanadate ions, though the degeneracy of the bands is not totally removed. In the high frequency region, there appear to be six to seven bands which are attributable to ν_1 and ν_3 stretching vibrations of VO_4^{3-} ions, by comparison to earlier work. In the bending region, the spectra are also suggestive of low site symmetries of the anion with incomplete resolution and are assigned to symmetric and asymmetric O–V–O bands, ν_2 and ν_4 [17].

Table 2
X-ray powder diffraction data for monoclinic $BaLaTh(VO_4)_3$

H	k	l	$d_{calcd.}$ (pm)	$d_{obsd.}$ (pm)	I/I_o
0	1	1	489	490	14
1	1	$\bar{1}$	440	440	25
1	0	1	423	423	11
1	1	1	366	366	25
2	0	0	342	342	58
1	2	0	323	323	100
2	1	0	310	309	10
0	1	2	300	301	60
2	0	$\bar{2}$	275	275	15
2	1	$\bar{2}$	258	257	17
1	1	2	254	254	7
1	3	0	230	229	7
1	0	$\bar{3}$	227	227	10
3	1	$\bar{1}$	224	224	10
2	2	1	220	220	10
2	1	2	203	203	17
1	3	$\bar{2}$	196.6	196.9	15
1	0	3	194.1	193.4	10
1	1	3	188.2	188.5	3
3	2	$\bar{2}$	185.4	185.5	13
3	0	$\bar{3}$	183.4	183.2	8
1	3	2	181.2	181.4	14
4	0	$\bar{1}$	176.8	177.0	7
4	0	0	170.8	170.6	7
4	1	0	166.3	166.4	6
2	1	3	161.9	161.5	7

Table 3
X-ray powder diffraction data for tetragonal $BaPrCe(VO_4)_3$

H	k	l	$d_{calcd.}$ (pm)	$d_{obsd.}$ (pm)	I/I_o
3	0	1	484	484	22
4	4	0	390	392	6
6	0	0	368	368	100
5	1	1	359	357	11
6	3	0	329	330	14
6	1	1	316	316	25
6	3	1	293	293	12
3	3	2	274	274	47
6	6	0	261	260	9
6	0	2	242	242	6
9	0	1	229	229	12
3	0	3	206	206	5
9	6	1	194.3	194.4	5
9	3	2	188.5	188.7	26
12	0	0	183.9	183.9	9
9	0	3	161.4	161.4	3
9	9	2	152.6	152.8	3
9	6	3	147.8	147.9	5

Table 4
Frequencies of infrared vibrational spectra of monazite type BaLnTh$(VO_4)_3$ compounds in cm^{-1} [a]

BaLaTh$(VO_4)_3$		BaPrTh$(VO_4)_3$		Assignments
		892	sh	ν_3 (antisymmetric stretching)
839	sh	840	s	
810	s	806	s	
780	sh	780	sh	
770	sh	766	sh	
750	w sh	752	sh	
735	sh	730	sh	
882	sh	880	sh	ν_1 (symmetric stretching)
478	w sh	479	sh	ν_4 (antisymmetric bending)
		430	sh	
421	m	420	m	
412	sh	410	w sh	
382	w	382	w	ν_2 (symmetric bending)
372	sh			
350	sh	352	sh	

[a] Abbreviations: m, medium; s, strong; sh, shoulder; v, very; w, weak.

Table 5
Frequencies of infrared vibrational spectra of the zircon super-structured BaLnCe$(VO_4)_3$ compounds, in cm^{-1} [a]

BaLaCe$(VO_4)_3$		BaPrCe$(VO_4)_3$		BaNdCe$(VO_4)_3$		BaSmCe$(VO_4)_3$		Assignments
899	sh	900	sh	898	sh	900	sh	ν_3 (antisymmetric stretching)
860	sh	861	sh	862	sh			
831	sh	830	sh	831	sh			
820	s	820	s	816	s	820	s	
782	sh	781	sh	785	sh	784	sh	
746	sh	744	sh	742	sh	740	sh	
		721	sh					
461	w sh	460	w sh	460	w sh	460	w sh	ν_4 (antisymmetric bending)
452	m	451	m	452	m	453	m	

[a] Abbreviations: m, medium; s, strong; sh, shoulder; v, very; w, weak.

The infrared spectra of BaLnCe$(VO_4)_3$ where Ln=La, Pr, Nd or Sm, show more than expected number of bands in the stretching region under D_{2d} (or perhaps lower) site symmetry approximation for the VO_4^{3-} ions, associated with zircon related structure [15,16,18,19]. The enrichment in the number of bands may probably be the result of either factor group splitting and/or some asymmetry in anions in the crystal lattice due to differences in environment, polarizing powers and charges of the multications present in the unit cell. In the bending region, the bands ~460 cm^{-1} and ~450 cm^{-1} are easily assigned to two split components of the degenerate ν_4 mode.

It is thus seen that the substitution of cerium for thorium at tetravalent site in the monoclinic BaLnTh$(VO_4)_3$ compounds resulted in superstructured zircon BaLnCe$(VO_4)_3$ compounds as expected.

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