Studies on Triple Orthovanadates. Part 3.[1,2] Crystal Chemistry of the Zircon Analogues of Type $M^{II}LnM^{IV}(VO_4)_3$ (M^{II} = Ca or Pb; M^{IV} = Ce or Th; Ln = Lanthanide element)

Mahadeo A. Nabar,* Bal G. Mhatre, and Alka P. Vasaikar
Department of Chemistry, University of Bombay, Vidyanagari, Bombay 400 098, India

The solid-state synthesis and crystallographic characterization of some triple orthovanadates with general formula $M^{II}LnM^{IV}(VO_4)_3$ (M^{II} = Ca or Pb; M^{IV} = Ce or Th) are presented. The compounds are found to crystallize with a tetragonal unit cell of space group $I4_1/amd$ and are isostructural with lanthanide orthovanadates ($LnVO_4$) having the zircon structure. Attempts are made to explain the stability range of the zircon structure on the basis of average ionic radii of substituting cations in the present group of triple orthovanadates.

In the evaluation of the crystal structure of anhydrous $LnXO_4$ (X = P, As, or V) it was found that these compounds can possess the monazite or xenotime (zircon-type) structure.[3-7] The reported data show that for each of these series of compounds the boundary between the monazite and xenotime structure occurs at a different rare-earth element. Carron *et al.*[8] established that the largest cation having the xenotime structure was Tb^{3+} in the case of phosphates, Sm^{3+} in the case of arsenates, and Ce^{3+} in the case of vanadates. These authors showed a quantitative relationship between the ionic radius of the largest xenotime-forming rare-earth element, B (formal six-fold ionic radii from Ahrens [9]) and the size of the anion, A (oxygen–central atom distance). Compounds with an A : B ratio above 1.86 should have the xenotime structure, whereas compounds having an A : B ratio below 1.86 should exhibit the monazite structure. Subsequent studies have shown that this boundary limit of anion to cation size ratio for the zircon–monazite transition could not be fixed to a single point, but there lies an overlapping range where in many cases, species exhibiting dimorphism could be obtained.

Double ortho-salts of the type $M^{II}Th(XO_4)_2$ (M^{II} = Cd, Ca, Sr, Pb, or Ba; X = P, As, or V) exhibiting zircon and monazite structures,[10] and those with formulae $M^{I}M^{IV}_2(XO_4)_3$ and $M^{II}M^{IV}(XO_4)_2$ (where M^{I} = Li or Na; M^{II} = Cd, Ca, or Sr; M^{IV} = Th, Np, or Pu; X = V) having the zircon structure,[11,12] were also found to agree with the above observation if B was taken to be the average size of cations present in the corresponding species. The triple orthovanadates, for example $CdLnTh(VO_4)_3$, with an A : B ratio above 1.86 are found to have the zircon structure,[1] those located on the borderline of zircon–monazite stability fields display the dimorphic phases.[2]

In the present work, the synthesis and lattice parameters of $M^{II}LnTh(VO_4)_3$ (M^{II} = Ca or Pb) and $CaLnCe^{IV}(VO_4)_3$ are reported. Repeated attempts to synthesize $PbLnTh(VO_4)_3$ (Ln = Tm or Yb) resulted in mixtures comprising $LnVO_4$ and $Th(VO_3)_4$. The synthesis of triple orthovanadates having cerium at tetravalent ion sites was mainly undertaken to assess its effect on the stability of the zircon structure in the present group of triple orthovanadates. It is interesting to note here that the earlier attempts to substitute tetravalent cerium at the thorium sites in $M^{II}Th(VO_4)_2$ compounds were unsuccessful.[13]

Experimental

The compounds under study were prepared using standard pyrotechniques, following mechano-chemical treatment of AnalaR grade reactants. The method consisted of treating stoicheiometric quantities of the nitrates of the respective di-, tri-, and tetra-valent elements [obtained from the corresponding oxides in the case of the lanthanides, carbonate in the case of calcium, and hydroxide in the case of cerium(IV)] with ammonium metavanadate in aqueous medium and mixing thoroughly for 1 h. The mixed products were dried, ground, and sintered 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 823—1 213 K, to obtain a high degree of crystallinity. The mechano-chemical treatment, *i.e.* intergrinding, pressing for disc-making, and sintering of mixed powder, was repeated several times to achieve homogeneous chemical composition. The completeness of the reaction was confirmed by *X*-ray diffraction.

The *X*-ray powder diffractograms were recorded on a Philips *X*-ray diffractometer PW 1009/30 NRD 1023, previously calibrated with silicon, using nickel-filtered copper radiation (λ = 1.5418 Å). The relative intensities, calculated by taking that of the highest peak as 100, and the *d*-spacings of $M^{II}LnM^{IV}(VO_4)_3$ compounds synthesized in the present study follow closely those observed for $LnVO_4$.[14,15] The structure must therefore conform to the atomic arrangement known as zircon type. Zircon-type crystals have symmetry $I4_1/amd$ (D_{4h}^{19}), as indicated by the systematic extinctions of reflections: hkl, $h + k + l = 2n + 1$; $hk0$, $h(k) = 2n + 1$; $0kl$, $k + l = 2n + 1$; hhl, $l = 2n + 1$, $2h + l = 4n + 1$.

Results

The lattice dimensions were refined using a least-squares method and are collected in the Table. The *c* : *a* ratios for all the compounds are within the range prescribed for the zircon structure by Vegard.[16] No discontinuity is observed in the alterations of the lattice parameters of these triple orthovanadates on substitution of cations with decreasing ionic radii at di-, tri-, and tetra-valent ion sites. The Figure shows the plots of unit-cell volumes against the ionic radii of rare-earths [17] for the three isomorphous series. (The eight-co-ordinated cations are considered here so as to be in harmony with the cation

Table. Unit-cell dimensions and other data for $\mathrm{M^{II}LnM^{IV}(VO_4)_3}$ complexes

Compound	a/Å	c/Å	c/a	U/Å^3	D_c/g cm^{-3}	D_m/g cm^{-3}
$\mathrm{PbLaTh(VO_4)_3}$	7.398(4)	6.541(6)	0.884	358.0	5.71	5.68
$\mathrm{PbPrTh(VO_4)_3}$	7.387(3)	6.553(4)	0.887	357.5	5.73	5.70
$\mathrm{PbNdTh(VO_4)_3}$	7.379(3)	6.525(4)	0.884	355.4	5.78	5.76
$\mathrm{PbSmTh(VO_4)_3}$	7.353(2)	6.506(4)	0.885	351.7	5.88	5.86
$\mathrm{PbGdTh(VO_4)_3}$	7.331(2)	6.491(3)	0.885	348.8	5.98	5.97
$\mathrm{PbTbTh(VO_4)_3}$	7.320(3)	6.475(5)	0.885	346.9	6.02	6.01
$\mathrm{PbDyTh(VO_4)_3}$	7.296(3)	6.459(5)	0.885	343.8	6.10	6.09
$\mathrm{PbHoTh(VO_4)_3}$	7.275(6)	6.446(8)	0.886	341.2	6.16	6.14
$\mathrm{PbYTh(VO_4)_3}$	7.272(6)	6.436(8)	0.885	340.3	5.68	5.64
$\mathrm{PbErTh(VO_4)_3}$	7.263(6)	6.437(9)	0.886	339.6	6.20	6.16
$\mathrm{CaLaTh(VO_4)_3}$	7.300(3)	6.457(5)	0.885	344.1	4.86	4.84
$\mathrm{CaPrTh(VO_4)_3}$	7.287(2)	6.440(3)	0.884	342.0	4.91	4.89
$\mathrm{CaNdTh(VO_4)_3}$	7.272(3)	6.425(5)	0.884	339.8	4.96	4.94
$\mathrm{CaSmTh(VO_4)_3}$	7.261(3)	6.434(4)	0.886	339.2	5.01	5.00
$\mathrm{CaEuTh(VO_4)_3}$	7.258(4)	6.431(5)	0.886	338.7	5.03	5.02
$\mathrm{CaGdTh(VO_4)_3}$	7.255(3)	6.437(6)	0.887	338.8	5.06	5.04
$\mathrm{CaTbTh(VO_4)_3}$	7.250(3)	6.433(5)	0.887	338.1	5.08	5.07
$\mathrm{CaDyTh(VO_4)_3}$	7.235(4)	6.415(9)	0.887	335.8	5.14	5.13
$\mathrm{CaHoTh(VO_4)_3}$	7.222(3)	6.411(6)	0.888	334.4	5.18	5.15
$\mathrm{CaYTh(VO_4)_3}$	7.218(3)	6.410(5)	0.888	333.9	4.68	4.66
$\mathrm{CaErTh(VO_4)_3}$	7.194(1)	6.386(2)	0.888	330.5	5.25	5.26
$\mathrm{CaTmTh(VO_4)_3}$	7.189(2)	6.378(2)	0.887	329.6	5.28	5.27
$\mathrm{CaYbTh(VO_4)_3}$	7.179(1)	6.373(2)	0.888	328.4	5.33	5.34
$\mathrm{CaLaCe(VO_4)_3}$	7.275(3)	6.433(4)	0.884	340.4	4.32	4.30
$\mathrm{CaPrCe(VO_4)_3}$	7.249(1)	6.407(2)	0.884	336.7	4.38	4.35
$\mathrm{CaNdCe(VO_4)_3}$	7.214(5)	6.372(7)	0.883	331.6	4.47	4.44
$\mathrm{CaSmCe(VO_4)_3}$	7.205(4)	6.373(5)	0.885	330.8	4.55	4.49
$\mathrm{CaEuCe(VO_4)_3}$	7.201(2)	6.377(2)	0.886	330.7	4.53	4.53
$\mathrm{CaGdCe(VO_4)_3}$	7.191(2)	6.369(3)	0.886	329.3	4.59	4.60
$\mathrm{CaTbCe(VO_4)_3}$	7.176(3)	6.362(4)	0.887	327.6	4.62	4.62
$\mathrm{CaDyCe(VO_4)_3}$	7.162(3)	6.352(4)	0.887	325.8	4.67	4.68
$\mathrm{CaHoCe(VO_4)_3}$	7.157(2)	6.350(3)	0.887	325.3	4.70	4.70
$\mathrm{CaYCe(VO_4)_3}$	7.150(3)	6.342(4)	0.887	324.2	4.19	4.18
$\mathrm{CaErCe(VO_4)_3}$	7.130(4)	6.323(5)	0.887	321.4	4.77	4.76
$\mathrm{CaTmCe(VO_4)_3}$	7.126(3)	6.321(5)	0.887	321.0	4.80	4.80
$\mathrm{CaYbCe(VO_4)_3}$	7.120(3)	6.321(4)	0.888	320.4	4.82	4.82

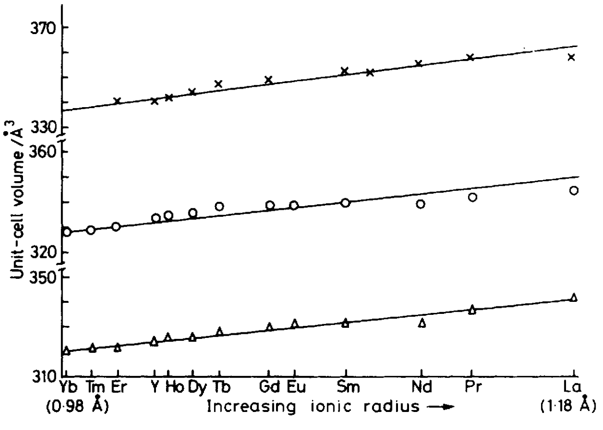

Figure. Plots of unit-cell volume *versus* eight-co-ordinated ionic radii of rare earths: $\mathrm{CaLnCe^{IV}(VO_4)_3}$ (△), $\mathrm{CaLnTh(VO_4)_3}$ (○), and $\mathrm{PbLnTh(VO_4)_3}$ (×)

arrangement in the zircon structure.[18,19]) The nature of these graphs clearly suggests that within a series, the volume is directly proportional to the ionic radii of the rare earths. The variation in the slopes is indicative of the fact that the extent of change in volume is also governed by factors such as differences in ionic radii of cations substituted in a compound and/or the physical properties of these ions, in addition to average ionic radii. A comprehensive study involving all possible substitutions at $\mathrm{M^{II}}$ and $\mathrm{M^{IV}}$ sites, which is in progress, could establish the stability domain of the zircon structure in relation to (*i*) upper and lower limits of average ionic radii, (*ii*) ratios of ionic radii of three substituting cations with one another, and (*iii*) some other physical properties of the substituted cations. It would be premature to reason the non-formation of $\mathrm{PbLnTh(VO_4)_3}$ (Ln = Tm or Yb) here.

Discussion

At the present stage of investigation, it can be stated that the compounds considered here could be derived from $\mathrm{LnVO_4}$ through the partial substitution of Ln as shown below,

$$3\mathrm{Ln} \longrightarrow \mathrm{M^{II}} + \mathrm{Ln} + \mathrm{M^{IV}}$$

and the possibility of synthesis and structural evolution of the $\mathrm{M^{II}LnM^{IV}(VO_4)_3}$ compounds is governed by the simple main condition that the size of the substituting cations should be approximately the same as that of the replaced rare-earth.

On the basis of the values obtained for the ratios of anion size to average size of substituted cations, *i.e.* A : B ratio in $\mathrm{M^{II}LnM^{IV}(VO_4)_3}$ compounds, a zircon structure could be predicted for all these compounds. It may be mentioned here that $\mathrm{PbLaTh(VO_4)_3}$ with an A : B ratio equal to 1.842 (1.691 for eight-co-ordination) exhibits dimorphic transformation from zircon to monazite.[2]

Acknowledgements

We thank the Tata Institute of Fundamental Research and the University Department of Computer Science for *X*-ray and computer facilities. Financial assistance (to B. G. M. and A. P. V.) by University of Bombay and University Grants Commission, India, is gratefully acknowledged.

References

1 Part 1, M. A. Nabar, B. G. Mhatre, and A. P. Vasaikar, *J. Appl. Crystallogr.*, 1981, **14**, 469.

2 Part 2, M. A. Nabar and B. G. Mhatre, *J. Solid State Chem.*, 1982, **45**, 135.

3 M. K. Carron, C. R. Naeser, H. J. Rose, jun., and F. A. Hildebrand, *U.S. Geol. Survey Bull.*, 1958, **1036-N**, 253.

4 M. Strada and G. Schwendimann, *Gazz. Chim. Ital.*, 1934, **64**, 662.

5 A. Durif and F. Forrat, *C. R. Acad. Sci. Ser. C.* 1957, **245**, 1636.

6 W. O. Milligan, L. M. Watt, and H. J. Rachford, jun., *J. Phys. Colloid Chem.*, 1949, **53**, 227.

7 A. Durif, *Acta Crystallogr.*, 1956, **9**, 471.

8 M. K. Carron, M. E. Mrose, and K. J. Murata, *Am. Mineral.*, 1958, **43**, 985.

9 L. H. Ahrens, *Geochim. Cosmochim. Acta*, 1952, **2**, 155.

10 H. Schwarz, *Z. Anorg. Allg. Chem.*, 1964, **334**, 175; 1965, **334**, 261.

11 M. Pages and W. Freundlich in, ' Plutonium and Other Actinides,' Proc. 5th Int. Conf., 1975, eds. H. Blank and R. Lindner, North Holland, Amsterdam, 1966, p. 205.

12 W. Freundlich, A. Erb, and M. Pages, *Rev. Chim. Miner.*, 1974, **11**, 598.

13 H. Schwarz, *Z. Anorg. Allg. Chem.*, 1965, **335**, 167.

14 *Nat. Bur. Stand.*, (*U.S.*), *Monogr.*, 1966, **25**, 18.

15 M. E. Escobar and E. J. Baran, *Z. Anorg. Allg. Chem.*, 1978, **441**, 273.

16 L. Vegard, *Philos. Mag.*, 1916, **32**, 65.

17 R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, 1969, **25**, 925.

18 J. A. Baglio and O. J. Sovers, *J. Solid State Chem.*, 1971, **3**, 458.

19 H. Feuss and A. Kallel, *J. Solid State Chem.*, 1972, **5**, 11.

Received 29th July 1982; *Paper* 2/1315