Studies on Triple Orthovanadates.
IV. Crystal Chemistry of the Solid Solutions Ca$_{1-x}$Ba$_x$LaTh(VO$_4$)$_3$*

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Considerable attention has been recently focussed on the lanthanon ortho-salts LnXO$_4$ (X = P, As, Cr(V) or V). Structurally, the simple lanthanon ortho-salts may be divided into two classes. These are the monoclinic monazite structure and the tetragonal zircon structure, with larger lanthanons crystallizing in the former [1–6]. A structural transition has been reported to occur with Tb, Pr and Ce(III) for phosphate, chromate(V) and vanadate, respectively, with a predicted break at Pm for arsenate. It has been further observed that the ortho-salts of lanthanons situated at the borderline exhibit temperature-sensitive dimorphism [7].

A quantitative relationship between the oxygen–central atom distance and the cationic radii (six-fold) has been reported, 1.86 being the highest value below which monazite structure occurs [2]. Multiple ortho-salts of the type M^{II}M^{IV}(XO$_4$)$_2$ [5, 6] and M^{I}M$_2^{IV}$-(XO$_4$)$_3$ [8–10] were also found to agree with this observation, when the average ionic radius of the cations present is considered.

The study on lanthanum-containing triple ortho-vanadates carried out in this laboratory brought out the facts that CaLaTh(VO$_4$)$_3$ [11] and BaLaTh-(VO$_4$)$_3$ [12] crystallize in zircon and monazite structures, respectively. On the other hand, SrLaTh-(VO$_4$)$_3$ (and PbLaTh(VO$_4$)$_3$) display dimorphism [13]. In order to extend our knowledge, a study of solid solution formation between calcium and barium triple orthovanadates, with a gradual change of composition, was undertaken.

Experimental

The solid solution series Ca$_{1-x}$Ba$_x$LaTh(VO$_4$)$_3$ was prepared following standard techniques and using AnalaR grade reactants. The compounds were obtained by addition of ammonium metavanadate solution to the desired metal nitrates in stoichiometric amounts in aqueous medium. The selected mole ratios were obtained by weighing appropriate quantities of calcium and barium carbonates for converting them to nitrates. The well-mixed solutions were evaporated to dryness, the residues were calcined initially at 573 K for 6 h and subsequently sintered at selected temperatures for 20–100 h in the form of well-pressed cylindrical pellets, with repeated cycles of grinding, pelleting and heating.

The X-ray powder patterns were recorded on a Philips X-ray diffractometer PW 1009/30 NRD 1023 using Ni-filtered copper radiation (λ = 1.5418 Å).

Results and Discussion

The experimental findings of successive substitution of calcium by barium in the triple orthovanadate solid solution series and the effect of temperature on the structural changes have been diagrammatically represented in Fig. 1.

CaLaTh(VO$_4$)$_3$ crystallizes as a zircon phase at 773 K. It can form solid solutions up to the composition Ca$_{0.6}$Ba$_{0.4}$LaTh(VO$_4$)$_3$ without disturbing the lattice. On raising the temperature to 1073 K, or even to 1473 K, however, the stability region for the solid solutions with zircon structure is contracted up to Ca$_{0.8}$Ba$_{0.2}$LaTh(VO$_4$)$_3$.

Subsequent progressive replacement of calcium by barium at 773 K up to the composition Ca$_{0.4}$Ba$_{0.6}$-LaTh(VO$_4$)$_3$ gives rise to a super-zircon structure, with tripling of the a-axis.

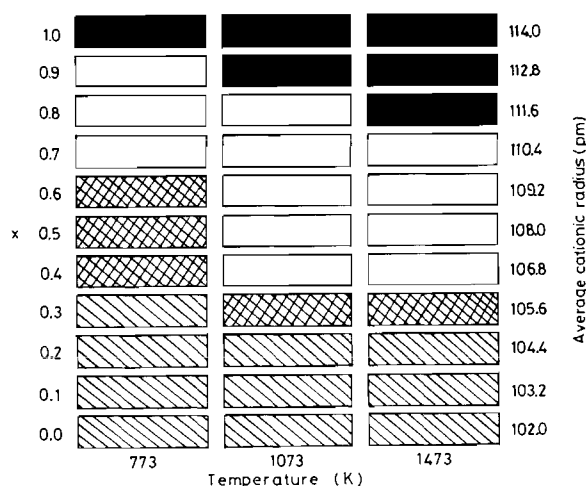Alternatively, BaLaTh(VO$_4$)$_3$, which has a monazite structure, cannot dissolve any CaLaTh-

Fig. 1. Structures of some phases in the Ca$_{1-x}$Ba$_x$LaTh-(VO$_4$)$_3$ system as a function of x at various temperatures: ▨ zircon; ▩ super-zircon; ■ monazite; □ mixed phase.

TABLE 1. Unit Cell Dimensions of Tetragonal and Monoclinic Phases of the $Ca_{1-x}Ba_xLaTh(VO_4)_3$ System at 1473 K

Structural type	Compound	a (pm)	b (pm)	c (pm)	β (°)	$V \times 10^6$ (pm³)
Zircon	$Ca_{1.0}Ba_{0.0}LaTh(VO_4)_3$	730.0 ± 0.3		645.7 ± 0.4		344.1
	$Ca_{0.9}Ba_{0.1}LaTh(VO_4)_3$	730.7 ± 0.4		645.6 ± 0.6		344.7
	$Ca_{0.8}Ba_{0.2}LaTh(VO_4)_3$	732.2 ± 0.2		647.0 ± 0.4		346.9
Super-zircon	$Ca_{0.7}Ba_{0.3}LaTh(VO_4)_3$	2192.3 ± 0.8		645.9 ± 0.4		3104.5
Monazite	$Ca_{0.2}Ba_{0.8}LaTh(VO_4)_3$	705.9 ± 0.5	730.7 ± 0.9	679.6 ± 0.7	104.90 ± 0.09	338.8
	$Ca_{0.1}Ba_{0.9}LaTh(VO_4)_3$	706.5 ± 0.5	731.9 ± 0.9	680.3 ± 0.7	104.93 ± 0.07	339.9
	$Ca_{0.0}Ba_{1.0}LaTh(VO_4)_3$	707.1 ± 0.5	732.4 ± 0.8	681.0 ± 0.6	104.96 ± 0.07	340.8

$(VO_4)_3$ to form a solid solution at 773 K. When the temperature is raised to 1073 K, monazitic solid solutions up to the composition $Ca_{0.1}Ba_{0.9}LaTh(VO_4)_3$ are formed. On raising the temperature further to 1473 K, a region of solid solutions expands up to the composition $Ca_{0.2}Ba_{0.8}LaTh(VO_4)_3$ without disturbing the structure.

A heterogeneous region, probably of two phases (namely, super-zircon and monoclinic structures) exists in between the compositions referred to above at the three selected temperatures. Particular interest was attached to the composition $Ca_{0.5}Ba_{0.5}LaTh(VO_4)_3$, where the average cation ionic radius is 108 pm [14]. Attempts to examine the temperature-dependent dimorphism, at least under the experimental conditions followed in the present work, remain unsuccessful; in this case in spite of the fact that the average cationic radii value lies well within the observed limit of 106 and 110 pm for lanthanum and other multiple vanadates [13].

The unit cell dimensions of the single phase compounds obtained at 1473 K are given in Table I. It can be seen that the volumes of the unit cells of the zircon and monazite structure, respectively, progressively change in accordance with the concentration of barium.

The available data indicate that in general the stability region of the solid solutions with zircon and related structures contracts with the rise in temperature. On the barium-rich side of the studies, however, the monazitic region of solid solution expands with the rise in temperature.

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