Crystal Data for Lanthanide Orthophosphates with the Zircon-Type Structure

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Results pertaining to the chemical and physical stability of borosilicate glass nuclear waste forms in aqueous environments have recently led to a number of reservations regarding the suitability of these materials for the long-term disposal of radioactive wastes. These reservations, in turn, have stimulated increased activity in evaluating single and polyphase crystalline materials as potential primary hosts for nuclear waste isolation. The lanthanide orthophosphates ($LnPO_4$ with Ln = La, Ce···Lu) represent one of the most promising new classes of crystalline materials for long-term, radioactive waste disposal [1–3].

Orthophosphates of the first half of the lanthanide series are structural analogs of monazite – a mineral that is known to have survived various natural weathering processes for two billion years. Since monazite ores often contain uranium and are the primary commercial source of thorium, the natural material has also been subjected to heavy particle radiation damage for extended periods of time. In contrast to natural zircons which can become fully amorphous as a result of similar natural radiation damage, however, monazites are always found in a crystalline (*i.e.*, nonmetamict) state in nature. This suggests that, in the case of monazite, natural geological processes have been sufficient to repair a significant portion of the structural damage produced by the inherent radioactivity. Since characteristics of this type are highly desirable in a primary nuclear waste form, a series of investigations of the chemical and physical properties of these materials has been undertaken.

An initial structural study was carried out for the monazite analog $CePO_4$ which was found to crystallize in the monoclinic $P2_1/n$ system with a unit cell consisting of irregular 9-coordinated cerium atoms linked together by distorted tetrahedral PO_4 groups [4]. Subsequent studies of the structure of

TABLE I. Unit-Cell Dimensions (Å) and Ionic Radii (Å) or Zircon-Type Lanthanide orthophosphates.

$LnPO_4$	a	c	$V^{1/3}$	Ref.	r*
Tb	6.940(1)	6.068(1)	6.636(1)	5	0.947
	6.941(3)	6.070(3)	6.638(3)	14	
Dy	6.907(2)	6.046(2)	6.607(2)	5	0.932
	6.917(3)	6.053(3)	6.616(3)	14	
	6.916(3)	6.048(3)	6.614(3)	15	
Ho	6.882(2)	6.025(2)	6.584(2)	5	0.917
	6.891(3)	6.031(3)	6.592(3)	14	
Er	6.860(1)	6.003(1)	6.562(1)	6	0.904
	6.864(3)	6.007(3)	6.565(3)	14	
	6.862(3)	6.008(3)	6.565(3)	15	
Tm	6.839(1)	5.986(1)	6.542(1)	6	0.892
	6.847(3)	5.994(3)	6.550(3)	14	
Yb	6.816(2)	5.966(2)	6.520(2)	6	0.880
	6.824(3)	5.980(3)	6.530(3)	14	
	6.812(3)	5.973(3)	6.520(3)	15	
Lu	6.792(2)	5.954(2)	6.500(2)	7	0.870
	6.798(3)	5.961(3)	6.507(3)	14	
	6.792(2)	5.955(2)	6.501(2)	16	

*Based on coordination number 8.

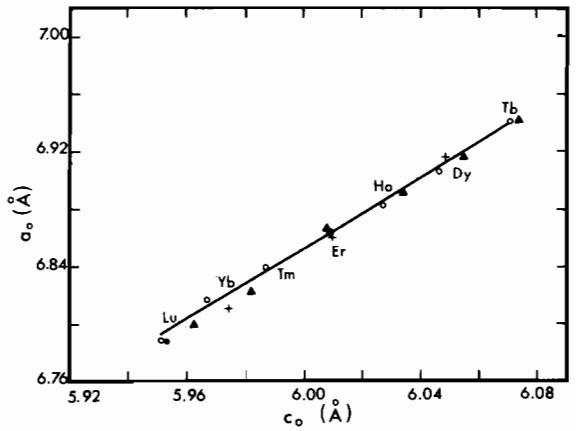

Fig. 1. Lattice constants a_o *vs.* c_o for the tetragonal zircon structure of rare-earth orthophosphates (see Table I). Plot was produced by Calcomp plotting. ○ Ref: 5, 6, and 7; ▲ Ref: 14; + Ref: 15; ● Ref: 16.

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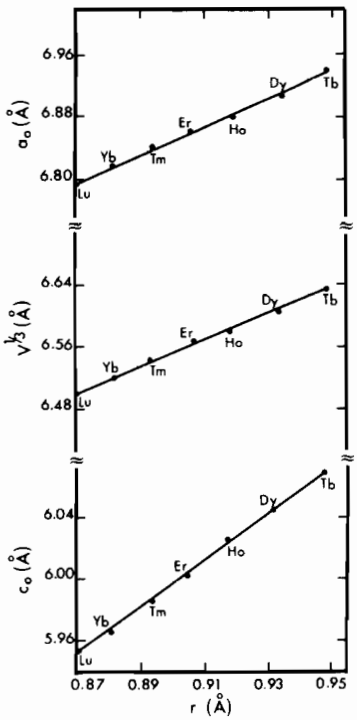

Fig. 2. Plots of a_o, cubic root of unit cell volume, and c_o *vs.* crystal radii [11] corrected to coordination number 8 (see Table II and text). Respective correlation coefficients (r) are: 0.9987, 0.9994, and 0.9996. Plots were obtained by Calcomp plotting.

the orthophosphates of Tb, Dy, Ho, Er, Tm, Yb, and Lu have shown that these compounds are described by the space group $I4_1/amd$ and have the tetragonal zircon structure [5–7]. The unit cell data for the zircon-structure orthophosphates have been compiled in Table I using results from several sources including our own previous work. As shown in Fig. 1, a plot of a *vs.* c yields a smooth linear curve as do the plots shown in Fig. 2 of a, c, and $V^{1/3}$ *vs.* the ionic radii of the corresponding lanthanides. The plots are similar to the results obtained for the hexagonal rare-earth trihydroxides [8] and rare-earth orthophosphates with the monazite-type structure [9, 10]. In an isotypic series of compounds such as the monazite or zircon structure lanthanide orthophosphates with a fixed anion, the volume of the unit-cell is proportional to the volume of the cations. Therefore, a striaght curve is expected from a plot of $V^{1/3}$ *vs.* the cation radius, assuming that these radii are sufficiently accurate. A linear curve was, indeed, obtained using the experimental ionic radii given by Templeton and Dauben [11]. The radii were corrected from coordination number 6 to coordination number 8 according to the treatment proposed by Pauling [12] and employing the assumption of a value of 12 for the Born exponent (ligancy 8, n = 12, correction factor 1.026). A linear regression analysis was applied to the plotted lattice parameters obtained from the work of Milligan *et al.* [5–7] (see Fig. 1). Once the linear regression curve was determined, a method of measuring the degree of association between the random variables (a and c) was applied. A correlation coefficient (r) of 0.9975 was obtained. In addition to a high linear correlation, the computation yielded homoscedasticity (s.d.'s were 0.039 and 0.047). Other cell parameters listed in Table I are also plotted in Fig. 1, but were not included in the regression analysis. Regarding Fig. 2, only the lattice constants from references, 5, 6, and 7 were plotted against the corresponding ionic radii. A least-squares straight line was fitted to the data and the resulting equations and standard deviations (σ) are given in Table II. Plots (not shown) using the ionic radii of Shannon [13], which are of an empirical nature, were also linear but were slightly scattered and produced inferior correlation coefficients.

TABLE II. Least-squares Linear Equations of a_o, c_o, and $V^{1/3}$ *vs.* Ionic Radii (r).

$a_o = (1.85591\ r + 5.18083)$ Å, $\sigma = 0.003$ Å
$c_o = (1.50301\ r + 4.64513)$ Å, $\sigma = 0.002$ Å
$V^{1/3} = (1.73118\ r + 4.99598)$ Å, $\sigma = 0.002$ Å.

Since the crystal data for the zircon structure lanthanide orthophosphates have not been systematically compiled and correlated previously, this task has been undertaken in the present work with the goal of providing a basis for future studies of heavy particle radiation damage in these materials.

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