

the fault configurations  $I_{0,\bar{0}}$ ,  $I_{0,\bar{1}}$ ,  $I_{0,\bar{2}}$  and  $I_{1,2}$  are enantiomorphous with  $I_{1,\bar{1}}$ ,  $I_{1,\bar{2}}$ ,  $I_{2,\bar{1}}$  and  $I_{2,0}$  respectively, leaving only 14 unique intrinsic fault configurations in the  $9R$  structure.

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## Cell Volumes of $AP\text{O}_4$ , $AV\text{O}_4$ , and $AN\text{bO}_4$ Compounds, where $A = \text{Sc, Y, La-Lu}^*$

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### Abstract

Precision lattice constants have been determined for a series of  $AP\text{O}_4$ ,  $AV\text{O}_4$ , and  $AN\text{bO}_4$  compounds (where  $A$  is a rare-earth ion, Sc, Y, or La) with the monazite, zircon, and fergusonite structures. The linear variation of the cube root of the unit-cell volume with the tabulated radius of the  $A$  ion [Shannon (1976). *Acta Cryst.* **A32**, 751–767] has been evaluated. Within the rare-earth series, only the Gd compounds have cell volumes which deviate from straight-line behavior, a result which implies that  $r_{\text{Gd}}$  (CN=8) should be  $1.196(1) \text{ \AA}$ . Systematic discrepancies are also noted for the corresponding Sc, Y, and La compounds which indicate that in these compounds the modified values of the radii should be  $r_{\text{Sc}} = 1.020(2)$ ,  $r_{\text{Y}} = 1.154(1)$ , and  $r_{\text{La}} = 1.313(2) \text{ \AA}$ . Literature cell constants have been used, in conjunction with the above analysis, to obtain radii for the analogous trivalent actinide ions,  $r_{\text{Pu}} = 1.250(5)$ ,  $r_{\text{Am}} = 1.237(5)$ , and  $r_{\text{Cm}} = 1.224(10) \text{ \AA}$ .

### Introduction

The concept of an ionic, or crystal, radius is still a most useful one in understanding the structures and stabilities of complex oxide phases. Shannon & Prewitt (1969) and Shannon (1976) have been able to develop, in part by an analysis of experimentally determined lattice constants and unit-cell volumes, a systematic series of empirical radii for different valence and coordination states. Muller & Roy (1974) have related the occurrence of specific crystal structures in complex oxide phases ( $A_xB_yO_z$ ) to these radii by use of the structure-field map, where a stability

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diagram is produced in which the coordinates of the phase space are the radii of the  $A$  and  $B$  ions.

As an initial phase of a program to focus in more detail on the concept of a structure-field map, precision lattice parameters have been determined for a series of  $A^{3+}P^{5+}O_4$ ,  $A^{3+}V^{5+}O_4$ , and  $A^{3+}Nb^{5+}O_4$  compounds where  $A$  is a rare-earth ion, scandium, yttrium, or lanthanum. Unit-cell volumes obtained from these lattice parameters have been analyzed in terms of the size of the  $A$  ion, and the results indicate that the radii of some of the  $A$  ions in these compounds may be different from the listed values (Shannon, 1976). Additional analysis of the unit-cell volumes of the analogous trivalent actinide compounds yields the corresponding radii of Pu, Am, and Cm in eightfold coordination.

The compounds used in this study were chosen, in part, because the structure-field map given by Muller & Roy (1974, Fig. 18) demonstrates a powerful systematization of the existing data, and because of the chemical and structural similarities between the phases that occur in this family of compounds. The monazite structure, which occurs primarily among the early lanthanide orthophosphates (prototype  $\text{CePO}_4$ ), is monoclinic, space group  $P2_1/n$ . The zircon structure (prototype  $\text{ZrSiO}_4$ ) is tetragonal, space group  $I4_1/amd$ , and occurs widely among the heavier lanthanide orthophosphates and arsenates, the lanthanide orthovanadates, and some actinide orthosilicates. The fergusonite structure (prototype  $\text{YNbO}_4$ ) is monoclinic, space group  $I2/c$ , and occurs among the lanthanide (and actinide) orthoniobates and tantalates. Each of the three structure types contains isolated  $\text{BO}_4$  tetrahedra interlinked by  $A$  ions which have primarily eightfold oxygen coordination. The structural and chemical similarities have been discussed elsewhere (Aldred, 1984).

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Table 1. *Lattice constants and unit-cell volumes for  $\text{APO}_4$  and  $\text{AVO}_4$  compounds with the monazite structure*

Numbers in parentheses in this and subsequent tables represent statistical uncertainties in least significant figures.

Compound	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\beta$ (°)	<i>V</i> (Å <sup>3</sup> )	<i>V</i> <sup>1/3</sup> (Å)
LaPO <sub>4</sub>	6.8402 (4)	7.0805 (5)	6.5064 (6)	103.34 (1)	306.62 (8)	6.7432 (6)
CePO <sub>4</sub>	6.7984 (5)	7.0234 (5)	6.4731 (5)	103.44 (1)	300.61 (8)	6.6989 (6)
PrPO <sub>4</sub>	6.7754 (9)	6.9879 (8)	6.4452 (8)	103.59 (1)	296.61 (12)	6.6690 (9)
NdPO <sub>4</sub>	6.7433 (5)	6.9590 (4)	6.4101 (4)	103.66 (1)	292.29 (6)	6.6365 (5)
SmPO <sub>4</sub>	6.6878 (6)	6.8943 (3)	6.3712 (5)	103.89 (1)	285.17 (7)	6.5822 (5)
EuPO <sub>4</sub>	6.6682 (8)	6.8654 (4)	6.3539 (5)	103.94 (1)	282.32 (7)	6.5601 (6)
GdPO <sub>4</sub>	6.6546 (6)	6.8486 (4)	6.3372 (6)	104.02 (1)	280.21 (8)	6.5438 (6)
LaVO <sub>4</sub>	7.0451 (4)	7.2840 (5)	6.7232 (2)	104.86 (1)	333.47 (7)	6.9346 (5)

### Experimental

The starting materials (at least 99.9% pure) were in the form of the normal sesqui- and pentoxides except for  $(\text{NH}_4)_2\text{HPO}_4$ . Lanthanum sesquioxide was obtained by decomposition of lanthanum oxalate at 1273 K. Dry powders ( $<64 \mu\text{m}$ ) were mixed under argon for 1d, compacted at 100 MPa, and heated slowly ( $50 \text{ K h}^{-1}$ ) in platinum containers to 1073 K ( $\text{AVO}_4$ ), 1373 K ( $\text{APO}_4$ ), or 1673 K ( $\text{ANbO}_4$ ) in pure oxygen. After an initial heat treatment for 2d, samples were quenched, ground, remixed, compacted and fired at the same temperature a minimum of two more times. Scanning electron microscopy with energy-dispersive X-ray analysis of selected samples showed homogeneous single-phase samples with no evidence of contamination by other elements (e.g. from the platinum container).

Diffraction scans were made on each sample by means of a GE XRD-5 instrument with Cu  $K\alpha$  radiation over the range  $2\theta = 10-120^\circ$ . Line widths were required to be comparable to the instrumental slit width and also to the line widths of standard samples ( $\text{CeO}_2$ , Si) as a criterion for complete reaction. All the phosphate samples had broader lines than the vanadate and niobate samples. Intensities of all observed lines were determined by peak height and compared with values listed in the Powder Diffraction File (1983) and values calculated by means of the *LAZY PULVERIX* computer program (Yvon, Jeitschko & Parthé, 1977). Very good agreement was obtained with the calculated intensities for the monazite-structured phosphates based on the atom positions determined for  $\text{CePO}_4$  by Beall, Boatner, Mullica & Milligan (1981). Good agreement was also obtained for the zircon-structured phosphates and vanadates although there was a tendency for preferred orientation [ $I_{\text{meas}}(h00) \gg I_{\text{calc}}(h00)$ ]. The agreement with the calculated intensities for the fergusonite-structured niobates, based on the atom positions determined for  $\text{LaNbO}_4$  and  $\text{NdNbO}_4$  by Tsunekawa & Takei (1978), was less good. Significant discrepancies were also observed with respect to intensities given in the Powder Diffraction File for some of the niobates.

Lattice parameters were obtained by Debye-Scherrer techniques at 298 (1) K with a 114.6 mm diameter camera and filtered Cr  $K\alpha$  radiation; standard least-squares extrapolation procedures were used (Mueller, Heaton & Miller, 1960).

### Results

Lattice constants and unit-cell volumes determined for the phosphate and vanadate compounds with the monazite structure are given in Table 1. The present results are in generally good agreement with the recently published values of Pepin & Vance (1981), and the values for  $\text{NdPO}_4$  and  $\text{EuPO}_4$  are in excellent agreement with those determined at the National Bureau of Standards (1974) and given in the Powder Diffraction File (1983). The agreement with the Powder Diffraction File for the other compounds is less good, particularly in the case of the monoclinic angle  $\beta$  for  $\text{SmPO}_4$  and  $\text{GdPO}_4$ .

The lattice constants obtained for the phosphate and vanadate compounds with the zircon structure are listed in Table 2. The data for the phosphate compounds are in reasonable agreement with the values from the Powder Diffraction File, except for the case of  $\text{YPO}_4$ , and to a lesser extent  $\text{YbPO}_4$ . A comparison of the *d* spacings and intensities reported by the National Bureau of Standards (1959) for  $\text{YPO}_4$  with the present results shows, in fact, excellent agreement. Further comparison with the calculated intensities from *LAZY PULVERIX* (Yvon *et al.*, 1977) indicates that several reflections were misindexed in the National Bureau of Standards report; in particular, the 323 should be the 204, the 314 should be the 512, the 523 should be the 424, and the 703 should be the 624. The origin for the smaller difference in the case of  $\text{YbPO}_4$  is less obvious. The present samples were prepared in pure oxygen and it is anticipated that all the Yb atoms are trivalent. The larger cell constants reported previously (Schwartz, 1963*a*) may be a reflection of the presence of some divalent Yb atoms which would have larger radii.

There is, generally, excellent agreement between the extensive data obtained by the National Bureau

Table 2. Lattice constants and unit-cell volumes for  $\text{APO}_4$  and  $\text{AVO}_4$  compounds with the zircon structure

Com- pound	$a$ (Å)	$c$ (Å)	$c/a$	$V$ (Å <sup>3</sup> )	$V^{1/3}$ (Å)
ScPO <sub>4</sub>	6.5759 (3)	5.7949 (3)	0.8812 (1)	250.59 (3)	6.3045 (3)
YPO <sub>4</sub>	6.8840 (3)	6.0202 (3)	0.8745 (1)	285.29 (4)	6.5831 (3)
TbPO <sub>4</sub>	6.9437 (4)	6.0743 (5)	0.8748 (1)	292.87 (6)	6.6409 (4)
DyPO <sub>4</sub>	6.9150 (2)	6.0488 (3)	0.8747 (1)	289.24 (3)	6.6133 (2)
HoPO <sub>4</sub>	6.8884 (2)	6.0281 (2)	0.8751 (1)	286.03 (3)	6.5888 (2)
ErPO <sub>4</sub>	6.8633 (9)	6.0087 (5)	0.8755 (2)	283.04 (10)	6.5657 (8)
TmPO <sub>4</sub>	6.8424 (6)	5.9895 (4)	0.8754 (2)	280.42 (7)	6.5454 (5)
YbPO <sub>4</sub>	6.8169 (6)	5.9715 (3)	0.8760 (1)	277.50 (6)	6.5226 (5)
LuPO <sub>4</sub>	6.7937 (2)	5.9582 (2)	0.8770 (1)	275.00 (2)	6.5029 (2)
ScVO <sub>4</sub>	6.7803 (5)	6.1349 (4)	0.9048 (1)	282.04 (6)	6.5580 (4)
YVO <sub>4</sub>	7.1193 (2)	6.2892 (2)	0.8834 (1)	318.76 (3)	6.8311 (2)
CeVO <sub>4</sub>	7.4013 (4)	6.4980 (3)	0.8780 (1)	355.96 (5)	7.0870 (4)
PrVO <sub>4</sub>	7.3640 (2)	6.4654 (2)	0.8780 (1)	350.61 (3)	7.0514 (2)
NdVO <sub>4</sub>	7.3315 (2)	6.4359 (2)	0.8778 (1)	345.94 (3)	7.0199 (2)
SmVO <sub>4</sub>	7.2654 (2)	6.3876 (6)	0.8792 (1)	337.18 (5)	6.9602 (3)
EuVO <sub>4</sub>	7.2373 (2)	6.3661 (3)	0.8796 (1)	333.45 (3)	6.9344 (2)
GdVO <sub>4</sub>	7.2131 (2)	6.3491 (2)	0.8802 (1)	330.34 (2)	6.9128 (2)
TbVO <sub>4</sub>	7.1770 (2)	6.3263 (3)	0.8815 (1)	325.86 (4)	6.8814 (3)
DyVO <sub>4</sub>	7.1480 (2)	6.3067 (3)	0.8823 (1)	322.23 (4)	6.8558 (3)
HoVO <sub>4</sub>	7.1237 (2)	6.2890 (4)	0.8828 (1)	319.15 (4)	6.8338 (3)
ErVO <sub>4</sub>	7.0973 (3)	6.2721 (2)	0.8837 (1)	315.94 (3)	6.8108 (3)
TmVO <sub>4</sub>	7.0693 (2)	6.2584 (2)	0.8853 (1)	312.76 (3)	6.7880 (2)
YbVO <sub>4</sub>	7.0439 (2)	6.2470 (2)	0.8869 (1)	309.94 (3)	6.7676 (3)
LuVO <sub>4</sub>	7.0263 (2)	6.2329 (2)	0.8871 (1)	307.71 (3)	6.7512 (2)

of Standards (1966, 1967) for the vanadate compounds with the zircon structure and the present results. Only in the case of  $\text{DyVO}_4$  are there significant differences between the lattice parameters, and they are of opposite signs so that the cell volumes agree well.

The lattice constants for the  $\text{ANbO}_4$  compounds with the fergusonite structure are listed in Table 3. Comparison with the parameters given for  $\text{LaNbO}_4$  and  $\text{YbNbO}_4$  by Brixner, Whitney, Zumsteg & Jones (1977), the only literature values reported to four decimal places, shows good agreement. The values given in the Powder Diffraction File (1983, see also McCarthy, 1971), with listed uncertainties of  $\pm 0.001 - 0.003$  Å in the cell parameters, are in only fair agreement with the present values.

### Discussion

Some observations about samples are initially in order. In the present work, every effort was made to use high-purity materials and react dry oxides together with no, possibly contaminating, additives or solutions. The possibility of stabilizing a phase by, for example, water of hydration, or impurities (as in the case of single-crystal preparation by the flux-growth method) is thus very remote. For some of the rare-earth vanadates and phosphates, the reported polymorphism, in the sense of different reported crystal structures for the same compound (e.g. Escobar & Baran, 1978; Bazuev, Zhilyaev & Shveikin, 1974; Kizilyalli & Welch, 1976), may well be associated with preparation techniques. Also, in the case of the compounds studied here, the lattice constants of

single-crystal samples are often in serious disagreement with those obtained for polycrystalline materials.

Shannon & Prewitt (1969) and Shannon (1976) have obtained a comprehensive series of ionic (or crystal) radii which are of significant use in the analysis of crystal structures. One of their techniques involves the presumption that in a series of isostructural and isovalent compounds with fixed coordination, e.g.  $A^{3+}B^{5+}O_4$ , a linear relationship exists between the cube of the cation radius  $r_A$  and the unit-cell volume  $V$ . Hawthorne (1978) has pointed out that the unit-cell volume of a crystal represents the cube of a complex sum of the cation and anion radii and therefore, in principle, the cell volume should not be a linear function of the cube of the cation radius, particularly over an extended range of values. This would be most evident, as noted by Hawthorne, for simple structures. As the structures become more complex, and it is not possible, in general, to write down a specific relation between the unit-cell volume and the cube of some sum of the cation and anion radii, the approximation of a linear variation should become better. With this caveat in mind we proceed to examine, on an empirical basis, the precision of the linear variation of  $V$  with  $r_A^3$  in the compounds studied here. Although the coordination around the  $A$  ion is eightfold in the tetragonal zircon structure (two  $A-O$  distances) and the monoclinic fergusonite structure (four  $A-O$  distances), it is ninefold in the monoclinic monazite structures (nine  $A-O$  distances). In the monazite compounds that have been studied by single-crystal X-ray diffraction to obtain atomic positions [ $\text{CePO}_4$  (Beall *et al.*, 1981),  $\text{LaVO}_4$  (Rice & Robinson, 1976), and  $\text{ThSiO}_4$  (Taylor & Ewing, 1978)], the largest  $A-O$  distance is always 0.2–0.3 Å greater than any other  $A-O$  distance. It would thus appear to be reasonable, in the present context, to treat the systematic variations of the cell volumes of the monazite-structure compounds in terms of the ionic radii for eightfold coordination, and thus facilitate comparison among the different structures.

A plot of the cube root of the cell volume  $V^{1/3}$  versus the crystal radius for the  $A$  ion in eightfold coordination  ${}^8r_A$ , as tabulated by Shannon (1976), is shown in Fig. 1. The open symbols represent the values given in Tables 1–3. The spread in literature values (Keller, 1962; Schwartz, 1963a; Brusset, Madaule-Aubry, Blanck, Glaziou & Laude, 1971; McCarthy, 1971; Rice & Robinson, 1976; Brixner *et al.*, 1977; Pepin & Vance, 1981; Powder Diffraction File, 1983) is shown by the vertical lines drawn through some of the data points; the remaining compounds have spreads smaller than the size of the symbol.

The solid lines in Fig. 1 represent the results of linear least-squares fits to the data from only the

Table 3. Lattice constants and unit-cell volumes for  $ANbO_4$  compounds with the fergusonite structure

Compound	$a$ (Å)	$b$ (Å)	$c$ (Å)	$\beta$ (°)	$V$ (Å <sup>3</sup> )	$V^{1/3}$ (Å)
YNbO <sub>4</sub>	5.2992 (3)	10.9485 (5)	5.0716 (2)	94.559 (6)	293.31 (5)	6.6442 (4)
LaNbO <sub>4</sub>	5.5667 (2)	11.5245 (4)	5.2020 (3)	94.084 (2)	332.88 (4)	6.9305 (3)
CeNbO <sub>4</sub>	5.5362 (3)	11.4126 (4)	5.1637 (3)	94.542 (4)	325.23 (5)	6.8770 (3)
PrNbO <sub>4</sub>	5.4962 (3)	11.3379 (9)	5.1579 (3)	94.528 (3)	320.41 (7)	6.8428 (5)
NdNbO <sub>4</sub>	5.4687 (3)	11.2811 (5)	5.1466 (3)	94.528 (4)	316.52 (5)	6.8150 (4)
SmNbO <sub>4</sub>	5.4182 (2)	11.1706 (3)	5.1184 (2)	94.662 (2)	308.76 (4)	6.7589 (3)
EuNbO <sub>4</sub>	5.3935 (4)	11.1301 (14)	5.1121 (3)	94.630 (1)	305.88 (8)	6.7378 (6)
GdNbO <sub>4</sub>	5.3715 (2)	11.0929 (10)	5.1062 (7)	94.562 (4)	303.29 (8)	6.7187 (6)
TbNbO <sub>4</sub>	5.3495 (3)	11.0386 (11)	5.0886 (3)	94.680 (6)	299.49 (5)	6.6905 (4)
DyNbO <sub>4</sub>	5.3238 (4)	10.9941 (6)	5.0815 (2)	94.626 (3)	296.45 (5)	6.6678 (4)
HoNbO <sub>4</sub>	5.3030 (2)	10.9555 (3)	5.0742 (2)	94.548 (3)	293.87 (3)	6.6484 (2)
ErNbO <sub>4</sub>	5.2814 (5)	10.9159 (8)	5.0642 (5)	94.542 (7)	291.04 (8)	6.6270 (6)
TmNbO <sub>4</sub>	5.2646 (3)	10.8794 (8)	5.0498 (3)	94.584 (4)	288.31 (5)	6.6062 (4)
YbNbO <sub>4</sub>	5.2429 (3)	10.8429 (10)	5.0456 (3)	94.496 (7)	285.95 (6)	6.5882 (4)
LuNbO <sub>4</sub>	5.2276 (2)	10.8216 (9)	5.0405 (2)	94.427 (5)	284.30 (4)	6.5754 (3)

rare-earth (Ce–Lu) series of isostructural compounds. Although the data follow this linear behavior quite well, careful examination shows small, but significant, systematic differences. This is illustrated in Fig. 2, where the difference between the observed and calculated radius for the least-squares fit,  $\Delta r_A$ , is plotted against  ${}^8r_A$ . Inasmuch as the values of  ${}^8r_A$  are given by Shannon (1976) to three decimal places, they have an implied precision of  $\pm 0.001$  Å. The deviations given in Fig. 2 are typically less than 0.001 Å and

thus illustrate the consistency between the tabulated radii values and the present unit-cell volumes. It should be emphasized that only with high-precision data can a rigorous examination of this type be carried out. The largest deviation ( $\sim 0.003$  Å and always of the same sign) for each of the series is in the case of Gd. To examine this effect more carefully, literature values were added to the data base for the least-squares analysis. They were chosen from the references listed in the previous paragraph on the basis that the study included a complete set of compounds prepared in a reproducible manner, and a weighting factor inversely proportional to the square of the quoted uncertainty was added. When these expanded data sets were reanalyzed, the same systematics persisted, *i.e.* the values for the Gd compounds deviated systematically from straight-line behavior. As a further check, appropriate literature values for the corresponding  $AAsO_4$  (zircon: Powder Diffraction File, 1983; Schwartz, 1963*a*),  $ACrO_4$  (zircon: Schwartz, 1963*b*; Buisson, Bertaut & Marschal, 1964) and  $ATAO_4$  (fergusonite: Keller, 1962; Powder Diffraction File, 1983) series were subjected to linear

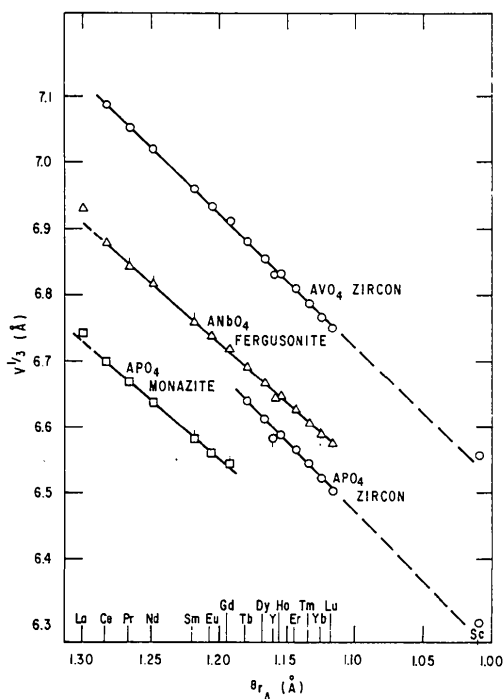


Fig. 1. Variation of the cube root of the unit-cell volume with size of the A ion in the  $ABO_4$  series indicated. Symbols: present data; vertical lines through the data points represent spread in literature values for given compounds. Heavy solid lines represent results of linear least-squares analysis of the data for the rare-earth compounds (Ce–Lu) only and dashed lines are an extrapolation of this fit.

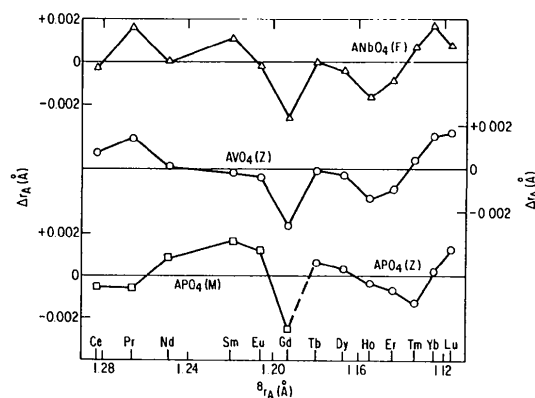


Fig. 2. Difference between the observed and calculated least-squares radius (see text and Fig. 1 for details) for the  $ABO_4$  series of compounds indicated; *F* fergusonite structure; *Z* zircon structure, *M* monazite structure.

least-squares analysis, and again systematic deviations were observed for the Gd compounds. It thus appears that for the structures studied here an appropriate Gd radius for CN=8 is 1.196 Å. This value was substituted into the various data sets and they were reanalyzed; in all cases a decrease in the root-mean-square (r.m.s.) error of 20–30% was observed.

It is evident from Fig. 1 that the cell volumes of the corresponding Sc, Y, and La compounds, when analyzed in terms of these least-squares fits, yield crystal radii which are internally consistent (*i.e.* independent of the *B* ion or the structure) but are different from the values given by Shannon. The modified radii values for Sc, Y, and La based on this analysis are given in Table 4 together with calculated CN=8 radii for the trivalent actinides Pu, Am, and Cm based on unit-cell volumes derived from literature lattice-parameter data (Bjorklund, 1958; Keller & Walter, 1965). Although the differences in the two sets of values for Sc, Y, and La are not large, in the sense of yielding an easily detectable change in *A*–O bond distance, they do represent changes in radii up to ten times larger than the implied precision of the Shannon & Prewitt values. Inasmuch as the yttrium value is based on an interpolation and the lanthanum value on a short extrapolation, they should be intrinsically more reliable than the scandium value which relies on a much longer extrapolation. Also, the observation noted earlier by Hawthorne (1978) with respect to linear behavior over wide data ranges should be kept in mind. It would, however, be difficult to conceive of a functional dependence of the cell volume with  $r_A$  which would fit both the rare-earth and lanthanum results (Fig. 1) with the Shannon & Prewitt value of  $r_{La} = 1.300$  Å.

The slopes of the  $V^{1/3}$  vs  $r_A$  lines in Fig. 1 represent the response of the unit-cell volume to systematic changes of ion size at the *A* site. It is evident that this slope is essentially constant for a given structure type and is larger for the more open tetragonal zircon structure than for either of the closer-packed monoclinic structures (monazite, fergusonite). Because of the limited number of *B* ions, the response of the cell volume to changes in *B*-ion size is more difficult to evaluate. The rate of change of cell volume with change in *B*-ion size for the zircon structure is again greater than for the monazite structure (Aldred, 1984). However, the numerical values are much smaller for the *B*-site substitution than for the *A*-site substitution. These results presumably reflect the tighter tetrahedral bonding around the *B* ion. For a given  $r_A$  and  $r_B$ , the cell volumes are in the order  $V_Z > V_M > V_F$  (*Z* = zircon, *M* = monazite, *F* = fergusonite) which is a reflection of the packing efficiency of the different structures. By comparison, ThSiO<sub>4</sub>, which can be prepared with both the monazite and zircon structures, shows a volume difference of 8% ( $V_Z > V_M$ )

Table 4. Modified CN=8 crystal radii for the listed *A* ions based on the unit-cell volumes of ABO<sub>4</sub> compounds; literature values (Shannon, 1976) given for comparison

A ion	B ion	Structures*	$r_A$ (Å)	$r_A$ (Shannon) (Å)
Sc	P, As, V	Z	1.020 (2)†	1.010
Y	P, As, Cr, V, Nb, Ta	Z, F	1.154 (1)	1.159
La	P, As, Nb	M, F	1.313 (2)	1.300
Gd	P, As, Cr, V, Nb, Ta	M, Z, F	1.196 (1)	1.193
Pu	P, As, Nb	M, F	1.250 (5)	—
Am	P, As, V, Nb, Ta	M, Z, F	1.237 (5)	—
Cm	P, Nb, Ta	M, F	1.224 (10)	—

\* *M* monazite, *Z* zircon, *F* fergusonite.

† Probable uncertainty.

between the two structures (Taylor & Ewing, 1978).

In summary, a careful assessment has been made of the variation of unit-cell volume with the crystal radii of the *A* (and to a lesser extent *B*) ion in a series of ABO<sub>4</sub> compounds with different structures and overall symmetries but the same near-neighbor site coordination. To a high accuracy, a linear variation of  $V^{1/3}$  with  $r_A$  is observed when *A* is a member of the rare-earth series (Ce–Lu), with the only significant (>0.001 Å) deviation being detected for Gd. On the other hand, the systematics of the present data and other literature results suggest that in the structures considered here the sizes of Sc, Y, and La are systematically different from the listed values by up to 0.013 Å. From published lattice constants of the corresponding actinide ABO<sub>4</sub> compounds, the crystal radii of Pu<sup>3+</sup>, Am<sup>3+</sup>, and Cm<sup>3+</sup> in eightfold coordination have been evaluated.

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## X-ray Diffraction Study on the Polytropic Structural Transformations Induced by Annealing in Cadmium Iodide Single Crystals

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### Abstract

The thermal transformations produced by annealing in  $\text{CdI}_2$  single crystals have been investigated. The mechanism of the structural changes has been analysed from the point of view of generation and/or elimination of two kinds of stacking faults of I–Cd–I molecular layers identified in the polytypic structure of  $\text{CdI}_2$ : faults *B* and *D*. It has been established that two thermal barriers for the nucleation of the structural changes in  $\text{CdI}_2$  may be distinguished: 353–383 and 463–503 K. The rules found for the polytypic transformation of  $\text{CdI}_2$  crystals allow one to predict the way in which a definite structure may transform by annealing.

### Introduction

Preparation of samples of desired structure remains one of the basic problems since polytypism was discovered 70 years ago. A complete list of the geometrical, chemical, thermodynamical and kinetic factors which determine the polytypic structure of a crystal is still not known. Two ways of controlled preparation of polytypic crystals are possible: controlled crystallization or modification of the structure of a crystal by inducing structural changes in the crystal.

Crystals growing at similar conditions, even in one crystallization run, may each have a different structure and single crystals with a uniform structure in the

whole volume form rather occasionally. Recently some papers have appeared on the effect of growth conditions on the polytypic structure of  $\text{CdI}_2$  (Gyaneshwar & Trigunayat, 1975; Sharma, Sharma & Agrawal, 1980; Jain & Trigunayat, 1980; Pałosz, 1980; Pałosz & Przedmojski, 1982*a, b*; Chaudhary & Trigunayat, 1982; Gierlotka & Pałosz, 1983), but the relations found experimentally between some of the crystallization factors and the structure of the crystals have a rather qualitative meaning. An alternative way of obtaining crystals with a uniform well defined structure is thermal transformation of polytypic crystals. In this case the conditions of crystal structure formation are easily reproducible: to repeat a given transformation process one needs to control the temperature and the time of annealing of the crystal. This process does not seem to be very sensitive to accidental factors such as impurities or thermal fluctuations, the influence of which on crystal growth may be very large. Polytropic transformations have been investigated many times for different polytypic materials (Baars & Brandt, 1973; Steinberger, Kiflawi, Kalman & Mardix, 1973; Minagawa, 1975; Verma & Trigunayat, 1976; Bind, 1978, 1979) but no conclusive study on the application of this method to control the crystal structure has been reported. To use transformation for the preparation of samples of a desired structure one should know the rules which govern this phenomenon; this will enable one to predict the structure which forms from a given initial structure upon heating at a defined temperature.