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CRYSTAL MORPHOLOGY OF THORIUM-BEARING SYNTHETIC MONAZITE

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ABSTRACT

Crystals of $CePO_4$ containing thorium and calcium and having the monazite structure have been synthesized by a fusion method in order to examine physical property changes related to variation in content of these cations. Goniometrical study shows that the principal habit-controlling forms in synthetic $CePO_4$ are $x\{\bar{1}01\}$, $m\{110\}$, and $e\{011\}$; also present are $b\{010\}$, $n\{120\}$, $l\{210\}$, $u\{021\}$, and $r\{111\}$.

The presence of thorium and calcium diadochically substituting for cerium in the structure induces marked changes in crystal habit. Twinning on $c\{001\}$ appears and is common. The previously-unreported forms $j\{313\}$ and $Y\{\bar{4}12\}$ are recognized, as are the rare $\lambda\{212\}$ and $\gamma\{041\}$. The proportions of three distinct habit types recognized in the thorium- and calcium-bearing crystals vary with the amount of thorium present. Twins on $c\{001\}$ are plentiful among crystals of low thorium content but are rare in samples containing the maximum amount of thorium (13.8 weight per cent ThO_2); platey crystals, tabular on $x\{\bar{1}01\}$, predominate among crystals of high thorium content.

From consideration of the effects upon axial ratio of other rare earth cations in the monazite structure, it is concluded that systematic morphological changes in natural monazite which might be expected as a consequence of differing thorium content could easily be masked by variations in proportions of rare earths.

INTRODUCTION

As part of an investigation of synthetic monazite, a study was made of the morphology of a series of cerium phosphate crystals containing thorium and calcium and having the monazite structure. The principal purposes of the over-all study were to examine the thorium-calcium charge compensation mechanism proposed for some natural monazites (Bowie and Horne, 1953; Frondel, 1958), and to determine the extent of changes in certain physical properties that might accompany variation in thorium content. The present paper deals only with observations made on the crystal morphology; other aspects of the work will be presented in another paper.

In order to isolate the physical-property changes resulting from the diadochic substitution of thorium and calcium in the trivalent cation site in the monazite structure and to minimize perturbative influences of other rare earth cations, the crystals were grown from cerium salts having very low content of rare earths other than cerium. Vacuum x-ray fluorescence analysis failed to reveal the presence of other rare earths, and, since all syntheses were made from the same stock rare earth salt, proportions of any trace quantities would be constant. Synthesis was achieved through a modification of the fusion method of Ouvrard (1888).

Precipitated ceric oxide fused with KH_2PO_4 in platinum at about 1000° C. for several days yielded crystals of size and quality suitable for morphological measurement. Thorium and calcium were introduced into the structure by mixing their fine precipitated oxides with the ceric oxide in the fusion. Crystal growth proceeds slowly, and runs of several days duration yielded some crystals nearly one millimeter in length.

The large observed variations of interfacial angles and axial ratios (Table 1) of monazites of different compositions have given rise to the reasonable inference that these variations are related to compositional differences (Dana's System of Mineralogy, 6th ed.). The series of synthetic cerium phosphate crystals of known thorium, calcium, and rare earth content should offer a controlled situation for testing this inference with respect to thorium content. However, single crystals examined from the different runs of crystals containing thorium and calcium proved unsuited by face quality or habit to careful goniometry and calculated axial ratios were not sufficiently precise for comparisons to be meaningful.

TABLE 1. COMPARISON OF AXIAL RATIOS AND BETA ANGLES OF SOME MONAZITES, $CePO_4$ AND $LaPO_4$

Material	Worker	Technique	$a:b:c$	β
$CePO_4$	Anthony	Morphology	0.9630:1:0.9185	103°32′
$CePO_4$	Mooney	Powder Method	0.9657:1:0.9200	103°38′
Monazite (Llallagua)	Parrish	Weissenberg	0.9660:1:0.9167	103°10′
Turnerite (Pardatsch)	Gliszczynski	X-ray (unspecified)	0.9698:1:0.9231	103°38′
Monazite (Milholland's Mill)	Dana	Morphology	0.96933:1:0.92558	103°40′
Monazite (Ishikawayama)	Ueda	Rotation-Oscillation	0.9685:1:0.9227	103°38′
Monazite	Miller; Dana, DesCloixeaux	Morphology	0.9740:1:0.9227	103°46′
Monazite	Trechmann	Morphology	0.9584:1:0.9217	102°42′
$(La, Ce)PO_4$ (La:Ce=1:1)	Anthony	Morphology	0.9573:1:0.9170	103°36′
$LaPO_4$	Mooney	Powder Method	0.9773:1:0.9191	103°34′

Because of the constancy of rare earth content, variation in the identity, number, and relative size of the crystallographic forms bounding the crystals—here called the crystal habit—should reflect changes in thorium and calcium content. No significant changes in habit of $CePO_4$

crystals grown at a number of temperatures within the range from 970° to 1050° C. were observed, so that, within the range of temperatures employed, temperature variation was not demonstrated to influence crystal habit. Sufficient familiarity with the variety of crystal habits in the different runs was gained by measurement of excellent $CePO_4$ crystals and selected better-quality crystals of the thorium-calcium runs to make possible recognition of significant crystal habits.

Reference was made to the extensive collection of illustrations of monazites in Goldschmidt's (1920) *Atlas der Krystallformen* for comparison of forms and habits of the mineral with those of the synthetic crystals. Minor forms identified during detailed measurement of these crystals are probably also present on many of those not measured; it was not thought necessary to report their presence, however, since little useful data would probably be gained from knowledge of their presence or absence.

The orientation of the crystals studied is in agreement with the structure cell (Gliszczynski, 1939; Parrish, 1939) and was confirmed by Weissenberg and precession photographs.

MORPHOLOGY OF RARE EARTH PHOSPHATES

Unlike the mineral, on which $a\{100\}$ predominates to the extent that crystals are very commonly tabular on it, $CePO_4$ exhibits a dominant habit controlled by the large development of $x\{\bar{1}01\}$. Figures 1c and 2 illustrate the typical development of the majority of these crystals. The a face, so important on natural crystals, is usually small or absent; $m\{110\}$ and $e\{011\}$ are the other principal, habit-controlling forms. These three forms are almost invariably present although m and e are usually of smaller development than x. Other forms identified, usually small and of little consequence in controlling habit, are: $b\{010\}$, $n\{120\}$, $l\{210\}$, $u\{021\}$, and $r\{111\}$. Table 2 lists the samples examined and the forms recognized. Table 3 presents the crystallographic elements calculated from measurements on a crystal having faces which gave excellent goniometrical signals.

Examination of the 119 drawings of monazite crystals in the *Atlas der Krystallformen* failed to reveal crystal habits similar to those of the $CePO_4$ grown in this study. As mentioned, this difference in habit reflects the small importance of $a\{100\}$ and the absence of $v\{\bar{1}11\}$ on $CePO_4$. Parker (1937), in his statistical analysis of the persistence of forms on monazite, found that $a\{100\}$ has the unusually high Niggli persistence number of 97, and that $v\{\bar{1}11\}$ is also very important with a persistence number of 81.5. m, x, and e, important on $CePO_4$, are the next three most abundant forms on the mineral having, respectively, persistence numbers of 75.5, 72.5, and 65.5. This consistent fundamental difference

TABLE 2. FORM ANALYSIS OF SYNTHETIC MONAZITE CRYSTALS

Sample Number	Wt. Per Cent ThO_2	Important Forms[1]					Comments on Habit and Habit Ratios
		m{110}	e{011}	x$\{\bar{1}01\}$	j{313}	Other	
$CePO_4$ (hydrothermally grown)	0	L	L	L		b{010}M	Equant; “3”;[2] no twins
$CePO_4$ (fusion grown)	0	L–M	L	L		b{010}M, r{111}S, n{120}S, l{210}S, a{100}M, μ\{130\}S, u{021}	“3” only; no twins
P-153	2.40	M	L	L	M		“1”≫“2” (approx. 2:1)
P-123	3.99	M–S	L	(L)	M		“1”≫“2”
P-131	4.28	M–S	L	(L)	M		“1”≫“2”
P-136	4.58	M–S	L	(L)	M		“1”≫“3”
P-124	4.69	M–S	L	(L)	M	γ\{041\}	“1”≫“3”
P-126	5.05	M–S	L	(L)	M		“1”≫“2”>“3”
P-121	5.62	M–S	L	(L)	M	$Y\{\bar{4}12\}$	“1”≫“2”
P-135	8.33	M–S	(L)	L	(M)	λ\{212\}	“3”>“1”
P-132	8.55	(M–S)	(L–M)	L	(M)		“3”>“1”=“2”
P-114	12.53	(M–S)	(L)–S	L	(M)		“2”>“3”; “1” rare
P-134	13.80	(M–S)	(L)–S	L	(M)		“2”≫“3”; “1” rare
P-160 (La:Ce=1:1)	0	M	M–S	L		$\sigma\{\bar{3}01\}$	“3”; no twins

[1] Use of parentheses about letter indicating importance of face—L=large, M=medium, S=small—indicates that the form enclosed is on the less-abundant habit type.

[2] See text for explanation of habit type symbols.

in habit is also seen in crystals of $CePO_4$ grown hydrothermally (Anthony, 1957). The common equant habit of crystals of this mode of growth is superficially similar to several crystals illustrated by Goldschmidt. The forms controlling the habit of hydrothermally grown $CePO_4$ are, however, x, m, and e.

TABLE 3. CRYSTALLOGRAPHIC CONSTANTS FROM MEASUREMENTS ON $CePO_4$

Monoclinic; prismatic—$2/m$
$a:b:c=0.9630:1:0.9185$
$p_0:q_0:r_0=0.9539:0.8930:1$

p_0' 0.9811; q_0' 0.9185
μ 76°28′; β 103°32′; x_0' 0.2407

Forms	Phi	Rho
b 010	0°00′	90°00′
a 100	90 00	90 00
n 120	28 06	90 00
m 110	46 53	90 00
l 210	64 55	90 00
e 011	14 41	43 31
x $\bar{1}01$	−90 00	36 31

Crystals of lanthanum phosphate were grown by the flux-fusion method but in all cases proved to be inferior in face quality and a study of their forms could not be made. The crystals are kite-shaped, apparently by extension on $x\{\bar{1}01\}$, and display subhedral development with, commonly, inferior curved crystal surfaces. Better crystals were obtained with runs containing both cerium and lanthanum. These crystals tend to be more equant in habit than either $CePO_4$ or $LaPO_4$, but display the same important forms, i.e. $e\{011\}$, $m\{110\}$, and $x\{\bar{1}01\}$ (Fig. 1b). The rare $\sigma\{301\}$ was observed on one crystal from sample P-160, the elements of which are presented in Table 4.

TABLE 4. CRYSTALLOGRAPHIC CONSTANTS FROM MEASUREMENTS ON $(La,Ce)PO_4$, WITH La:Ce=1:1 (SAMPLE P-160)

Monoclinic; prismatic—$2/m$
$a:b:c=0.9573:1:0.9170$
$p_0:q_0:r_0=0.9579:0.8913:1$

p_0' 0.9856; q_0' 0.9170
μ 76°24′; β 103°36′; x_0' 0.2420

Forms	Phi	Rho
m 110	47°04′	90°00′
e 011	14 47	43 29
x $\bar{1}01$	−90 00	36 38
σ $\bar{3}01$	−90 00	69 47

MORPHOLOGY OF CRYSTALS CONTAINING THORIUM AND CALCIUM

Introduction of thorium and calcium into the structure of $CePO_4$ induces a crystal habit change observed in all runs made. Principally, this change consists of the appearance of a twin on $c\{001\}$, and the development of forms not recognized on the thorium-free material. Twinning on $c\{001\}$ of the mineral is reported as being rare in Dana's *System of Mineralogy*, 7th edition, and is not mentioned in the 6th edition. Since the only known compositional difference between these twinned crystals and the rare earth phosphate crystals previously described is the presence of thorium and calcium, the twinning must be induced by their presence in the monazite structure.[1] Sample P-121, selected for measurement to illustrate the characteristic habit of thorium-bearing crystals is shown in Figs. 1a and 3. There is a general similarity to

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[1] Although temperatures of growth were different for individual runs, as previously noted, ranging from a high of 1050° C. to a low of 970±ca. 10°, there is no systematic relationship between thorium content and temperatures at which growth took place, so that temperature is not believed to be a factor in governing the crystal habits present.

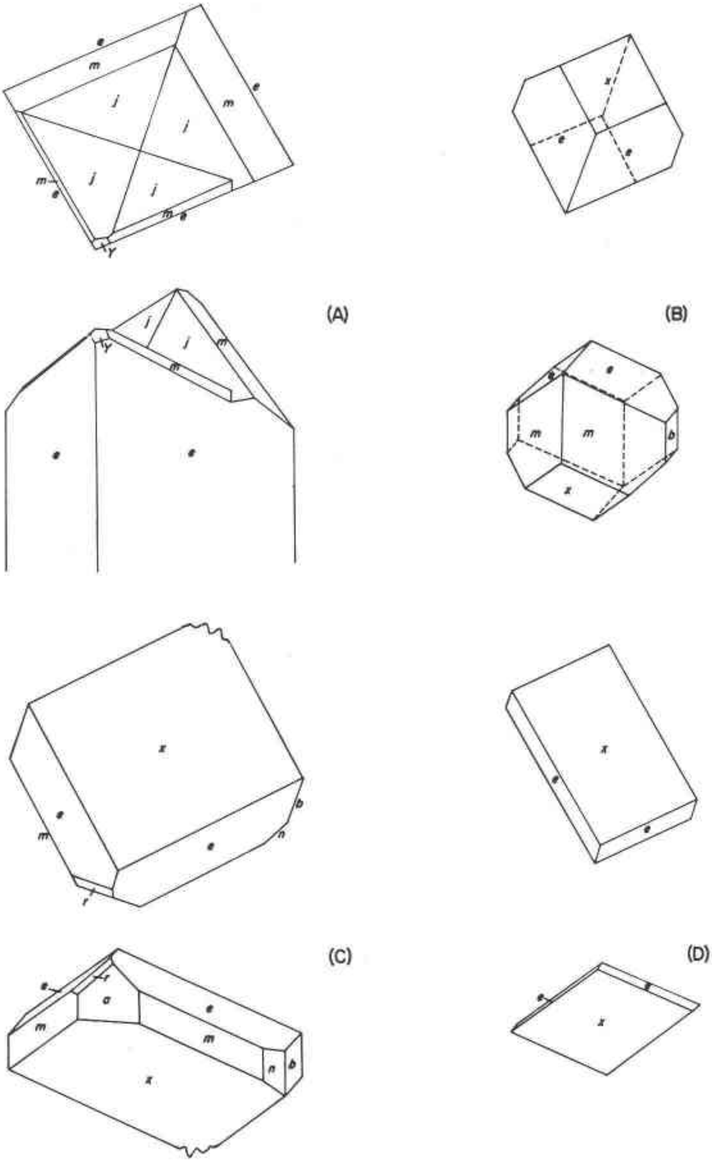

FIG. 1. Axonometric and orthographic drawings of synthetic monazite crystals. (A) Sample P-121, containing 5.62 weight per cent ThO$_2$; the *a* crystallographic axis is polar; twin plane is $c\{001\}$. (B) Sample P-160, non-thorium-bearing with Ce:La = 1:1. (C) CePO$_4$, non-thorium-bearing. (D) Sample P-114, containing 12.53 weight per cent ThO$_2$.

natural monazites elongated by development of *v*{$\bar{1}11$}, as illustrated in the *Atlas der Krystallformen*, Figs. 60, 62, 63, 91, 116, and 117. Elongation of the synthetic twinned crystals is, in contrast, always by extension of *e*{011}. Measurement of these crystals for purposes of calculating crystallographic elements is interfered with by the fact that faces in the terminal reentrants are almost invariably curved or are composites of a myriad of vicinal forms. The particular crystal illustrated was one which provided sufficiently good-quality signals of faces within the reentrant to permit indexing. The previously unreported form {313}, designated "*j*," proved to be the important terminal form. This form was not confirmed by measurement of good faces on any other crystal, but the general similarity of slope of the reentrant and the position of relatively poor signals suggest that *j*{313} or closely allied tautozonal forms are involved. Y{$\bar{4}12$}, also previously unreported, was noted on sample P-121. The rare λ{212} was identified on a twinned crystal of sample P-135, and γ{041} on P-124.

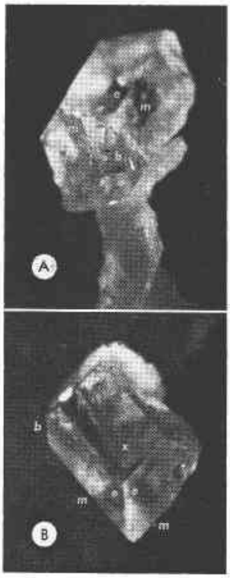

FIG. 2. $CePO_4$ crystal viewed (A) down [010], and (B) parallel to *c*. ×70.

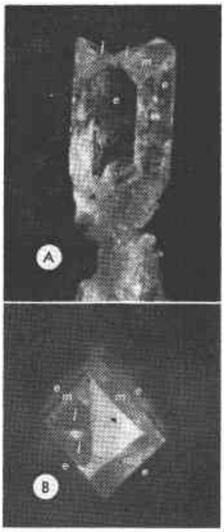

FIG. 3. Twinned synthetic monazite crystal containing 5.62 weight per cent ThO_2 (sample P-121). Elongation is by extension of e{011}; *a* polar (A) ×63; (B) ×80.

Examination of the thorium-containing series of synthetic crystals revealed that three habits predominate:

1. Crystals twinned on *c*{001} and elongated on *e*{011}, having a square-appearing cross section (Fig. 1a); 2. thin, rhombic-shaped crystals, tabular on *x*{$\bar{1}01$}, with small bounding

faces of *e* or *m*, or both (Fig. 1d); and 3. a thick but somewhat tabular habit controlled by extension of $x\{\bar{1}01\}$, with moderate development of *e* and *m*, together with minor development of $b\{010\}$, $\mu\{130\}$, $n\{120\}$, $l\{210\}$, $\gamma\{041\}$, and $r\{111\}$ (Fig. 1c). For convenience of reference in the following discussion, these habits will be designated "1," "2," and "3," respectively.

Study of all analyzed samples revealed a distinct trend in the proportions of these habits with changing content of thorium and calcium in the rare earth structural site. This trend is depicted in Fig. 4. No statistical counts were made to obtain quantitative data; the diagram, in which the slopes have no quantitative significance, serves only to illustrate the trend. All the thorium-bearing runs show the presence of twinned crystals of habit "1." The quantity of crystals of this habit relative to the other habits present increases initially as the thorium content increases. The predominant additional habit in those samples having relatively low thorium content is that of "2," so that the ratio "1":"2" increases with increasing thorium content. This ratio is greater than unity even in the crystals of lowest thorium content.

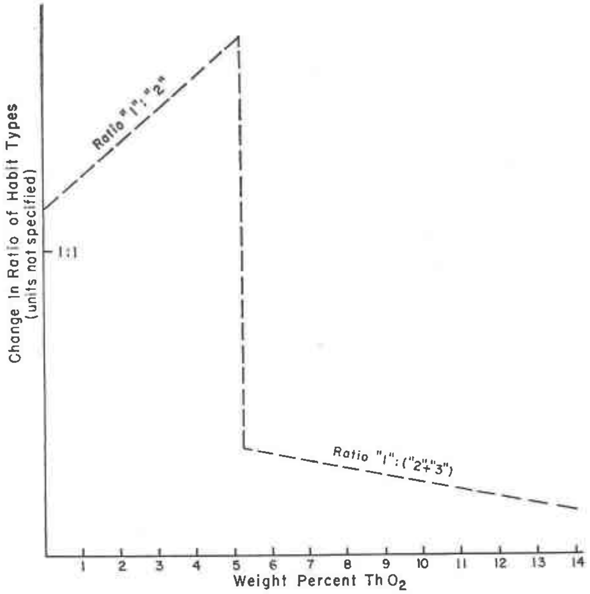

FIG. 4. Trends of habit variation with changes in thorium content of synthetic monazite crystals.

There is an abrupt reversal of this ratio when the thorium content exceeds the range of about 5 weight per cent thorium expressed as ThO_2. In crystals containing slightly more than about 5 weight per cent

ThO_2, habits "1" and "2" are about equal in quantity, but habit "3" appears and is more abundant than habits "1" and "2" combined. With increasing thorium content habit "1" becomes less abundant until twinned crystals are rare in samples having the highest thorium content. Table 2 presents the data on which these observations are based. An interesting but unexplained point in this connection is the presence of a hiatus at about that thorium content immediately below which there is a pronounced clustering of samples having similar thorium contents (between about 4 and 6 per cent ThO_2). A maximum for the habit ratio "1":"2" exists in this range of thorium content. Crystals containing more thorium show an abrupt change in the habit ratio with habit "2," initially less abundant than habit "3," becoming more plentiful until crystals having the highest thorium content consist largely of habit "2." The quantity of crystals of habit "1," relatively low on the high-thorium side of the hiatus, becomes smaller with increasing thorium content until they are rare in the sample having the highest thorium content.

INFLUENCE OF RARE EARTH CATIONS ON MORPHOLOGY

To anticipate the nature and magnitude of crystallographic changes which might be attendant upon variation of rare earth content in synthetic monazites, calculations were made using data derived by Mooney (1948) from four rare earth phosphates having the monazite structure. These data, obtained by the powder method on rare earth phosphates precipitated from aqueous solutions, are reproduced in Table 5 together with axial ratios and calculated values of the angle $m \wedge m'''$ derived from them.

Figure 5 is a plot of cell size variation against the trivalent radii of the rare earth cations (Ahrens, 1952) of the four phosphates. The general parallelism of slopes of the three curves indicates that the unit cell expansion due to increase in cation size is fairly uniform in the three axial directions. If the reversals in beta are real, there could not be a regular systematic change of interfacial angles in this series because of

TABLE 5. UNIT CELL PARAMETERS OF FOUR RARE EARTH PHOSPHATES,[1] AXIAL RATIOS, AND CALCULATED VALUES OF $m \wedge m'''$

XPO_4	a	b	c	β	Axial Ratio	$m \wedge m'''$
$LaPO_4$	6.89 ± .08	7.05 ± .02	6.48 ± .02	103°34′ ± 15′	0.9773:1:0.9191	87°04′
$CePO_4$	6.76	7.00	6.44	103°38′	0.9657:1:0.9200	86°22′
$PrPO_4$	6.75	6.94	6.40	103°21′	0.9726:1:0.9222	86°40′
$NdPO_4$	6.71	6.92	6.36	103°28′	0.9697:1:0.9191	86°38′

[1] Data from Mooney (1948).

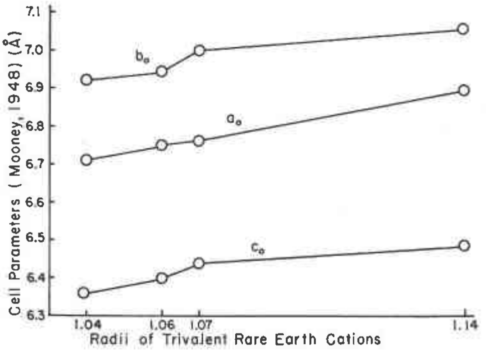

FIG. 5. Unit cell parameters of Mooney (1948) plotted against ionic radii of four trivalent rare earth cations.

the marked influence of beta on them. This effect is illustrated in Fig. 6 in which $m \wedge m'''$ is plotted against the same ionic radii.

Recent detailed work on Malayan alluvial monazites supports the supposition that the influence on crystallographic parameters due to variation in proportions of rare earths in natural monazites would probably mask morphological parametral changes which might otherwise reflect differences in thorium content. Flinter and coworkers (1963) were not able to detect systematic relationships between physical properties and thorium content, but did demonstrate expansion of certain interplanar spacings related to increase in the ratio of the large lanthanum ion to the sum of several small cations, specifically, La: (Sm+Gd+U+Y).

This work is based on a portion of a Ph.D. thesis presented to Harvard University; a paper on other aspects of the study is in preparation. I

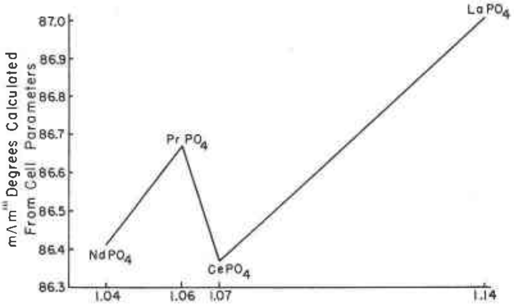

FIG. 6. Calculated interfacial angle $m \wedge m'''$ plotted against ionic radii of four trivalent rare earth cations.

wish to thank Professor Clifford Frondel for suggesting the general problem upon which this work was based and for helpful advice throughout the course of the study.

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