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THE CRYSTAL STRUCTURE OF CHERALITE

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ABSTRACT

The structure of cheralite, a thorium, calcium, rare earth monazite, has been completely redetermined. Patterson sections and three-dimensional difference maps were used to determine the atomic positions, and least squares refinement of the data reduced the *R*-factor to 0.084.

This structure is in accord with three of four previous monazite structure analyses, and the crocoite structure analysis. A relationship is apparent between increase of long Ce—O bonds and decrease of short Ce—O bonds and P—O bonds.

INTRODUCTION

Recent interest in monazite has focused on wide variations in composition and on a final determination of its correct structure. Many unit cell data have been accumulated for natural and synthetic monazite-type compounds (Mooney-Slater, 1962; Shankar and Khubchandani, 1956; Khubchandani, 1956; Bowie and Norne, 1953; Pabst, 1951; Parrish, 1939) and the data suggest no major structural change with cation changes in monazites. Anthony (1965) has observed, however, that cation changes do affect the morphology and twinning in monazites.

The crystal structure of monazite was first determined by Kokkoros (1942) from single crystal data. This determination was followed by that of Mooney (1948) from powder data. The two independent determinations are similar except for minor differences in positional parameters (see Mooney-Slater, 1962). In both cases the cation positions were deduced from intensities and the phosphate group positions were assigned in the intercation voids.

Ueda (1953) redetermined the structure of monazite by trial and error. His positional parameters disagree with those given by Kokkoros (1942) and Mooney (1948). The new mineral huttonite, $ThSiO_4$, was descirbed as the monoclinic dimorph of thorite by Pabst (1951) who stated that huttonite because of its powder pattern, unit cell dimensions and space group similarities was isostructural to monazite. No atomic positions were determined for huttonite. Quareni and Di Pieri (1965) have published a refinement of the structure of crocoite, $PbCrO_4$, a mineral that is also isostructural to monazite but the atomic parameters they give do not agree with those found by Kokkoros (1942) and Mooney (1948) but rather are similar to those given by Ueda (1953). More recently, Ghouse

(1965) has presented a structure determination of an Indian monazite and again there is considerable disagreement with the four previous determinations.

The state of the monazite structure therefore warrants clarification and it is the purpose of this paper to present the results of a three-dimensional structure analysis and refinement of cheralite, a member of the monazite family of minerals, to aid in this clarification.

EXPERIMENTAL

Cheralite bears a close resemblance to monazite in all of its morphological, optical and structural properties. It is however, significantly different from normal monazite, $CePO_4$, in composition. Cheralite normally contains calcium, thorium, uranium and lanthanides as major cationic constituents. A complete chemical analysis of cheralite was made by Mr. H. Ochs of Denver, Colorado as part of this study. The results are given in Table 1 together with the analysis of a cheralite by Bowie and Horne (1953). Both samples are from the same locality, Travancore, India.

TABLE 1. CHEMICAL ANALYSES OF CHERALITE
Weight percent

	(1)	(2)
Ce_2O_3	10.00	14.21
La_2O_3	9.15	
Y_2O_3	.30	13.35
ThO_2	36.25	31.50
CaO	7.45	6.30
PbO	.95	.92
U_3O_8	5.82	4.05
Fe_2O_3	.05	trace
P_2O_5	28.67	26.80
SiO_2	.88	2.10
H_2O	.05	.06
Total	99.57	99.29

[1] Plus other rare earth oxides.

(1) Chemical analysis of cheralite for this paper by H. Ochs.

(2) Cheralite analysis, Bowie and Horne (1953).

Formula for (1):

$$(\mathrm{Ce}_{0.580}\mathrm{La}_{0.532}\mathrm{Y}_{0.012}\mathrm{Th}_{1.304}\mathrm{Ca}_{1.260}\mathrm{Pb}_{0.040}\mathrm{U}_{0.196})_{3.924}(\mathrm{P}_{3.836}\mathrm{Si}_{0.140})_{3.976}{}^{0}{}_{16}$$

The unit cell and space group of our cheralite was determined from data collected from precession photographs (Rao and Finney, 1965). Cheralite is monoclinic, space group $P2_1/n$ and has the following unit cell dimensions: $a=6.717$, $b=6.920$, $c=6.434$ Å, all ± 0.005 Å, $\beta=103°50'\pm 5'$. The unit cell volume is 290.4 Å^3. The measured density is 5.20 g/cm^3 and the unit cell formula is $4(XPO_4)$ where X signifies the large cation.

Data were collected by means of multiple film pack Weissenberg equi-inclination photographs taken with Mo(Kα radiation of the zero through second level about the *a* and *c* axes and the zero and first level about the *b* axis. Absorption corrections for spherical crystals were applied to all data as well as corrections for Lorentz-polarization and spot separation due to α_1-α_2 resolution. Intensities were estimated visually.

STRUCTURE DETERMINATION

The structural problem was handled as if the structure was unknown. The location of the "cerium" and phosphorus atoms was accomplished by interpretation of Patterson sections. A study of a set of three-dimensional Fo-Fc(Ce+P) maps allowed unequivocal location of all oxygen atoms. At this stage of the determination the *R*-factor was 0.176.

Refinement was accomplished by use of a full matrix least-squares program modified by the senior author after a program in use at the Los Alamos Scientific Laboratory. Computations were carried out at the Colorado University Computer Center on the IBM 709 and 7044 computers.

The scattering factor for the "cerium" atom was determined by taking a weighted average of all atoms occupying the X position. Oddly enough, the atomic number of this weighted average is 58, that of cerium. All scattering factors were applied in the nine parameter exponential form, the values being those of Cromer, Larson and Waber (1963).

Five least-squares cycles were run utilizing eight scale factors, one for each reciprocal level as well as six isotropic temperature factors and eighteen positional parameters. All parameters were allowed to vary simultaneously. Initial refinement was ceased when positional parameter shifts became less than the standard deviations. Two additional cycles were then run to allow settling of oxygen temperature factors in the presence of the heavy atoms. At this point the *R*-factor was 0.092.

A second stage of refinement was then undertaken in which all duplicate reflections were removed and the data set placed on a single absolute scale. Two additional cycles were run using the single data set. This set contained 615 unique observed reflections out of a total of 907. During these cycles the weight used was: $Fo \leq 30$, $w=Fo/30$; $Fo \geq 80$, $w=80/Fo$. Where $30 < Fo < 80$, $w=1.0$. Structure amplitudes of unobservable reflections were assigned values of one-half the minimum observable limit for comparison purposes with calculated values but were excluded from the refinement. The final R-factor is 0.084 for the observable reflections only. The final positional parameters, isotropic temperature factors and standard deviations are listed in Table 2, together with the atomic positions of Mooney (1948), Ueda (1953), Ghouse (1965), and of Quareni and Di Pieri (1965) for crocoite. Structure factor data for cheralite is available upon request to the senior author.

TABLE 2. POSITIONAL PARAMETERS FOR MONAZITE AND CROCOITE

Thermal parameters and standard deviations, in parentheses, are given for cheralite only. All space groups are $P2_1/n$.

Atom		Cheralite	Monazite			Crocoite
		Finney & Rao Present Study	Ueda (1953)	Mooney[1] (1948)	Ghouse (1965)	Quareni & DiPieri (1965)
Ce	x	.2198(2)	.225	.208	.216	.2218 (Pb)
	y	.1596(2)	.147	.156	.160	.1450
	z	.3991(2)	.400	.417	.103	.3974
	B	1.08(2)Å^2				
P	x	.1960(8)	.206	.208	.221	.2010 (Cr)
	y	.1630(9)	.172	.156	.164	.1651
	z	.8858(9)	.894	.919	.599	.8800
	B	.83(7)				
O(1)	x	.2473(36)	.167	.211	.270	.2534
	y	.5064(38)	.514	.490	.505	.4982
	z	.4426(37)	.428	.423	.058	.4540
	B	2.56(41)				
O(2)	x	.0238(32)	.019	.033	.040	.0354
	y	.1044(30)	.128	.070	.121	.0989
	z	.6906(33)	.681	.735	.747	.6944
	B	1.84(30)				
O(3)	x	.3740(29)	.369	.384	.369	.3887
	y	.2221(28)	.250	.235	.190	.2173
	z	.7898(31)	.767	.820	.810	.7810
	B	1.56(27)				
O(4)	x	.1114(30)	.119	.126	.147	.1247
	y	.3337(35)	.319	.323	.353	.3461
	z	−.0011(31)	.042	.036	.440	−.0131
	B	1.93(28)				

[1] Mooney's (1948) original parameters have been transformed by $\frac{1}{2}-x, y, \frac{1}{2}-z$ for presentation in this table.

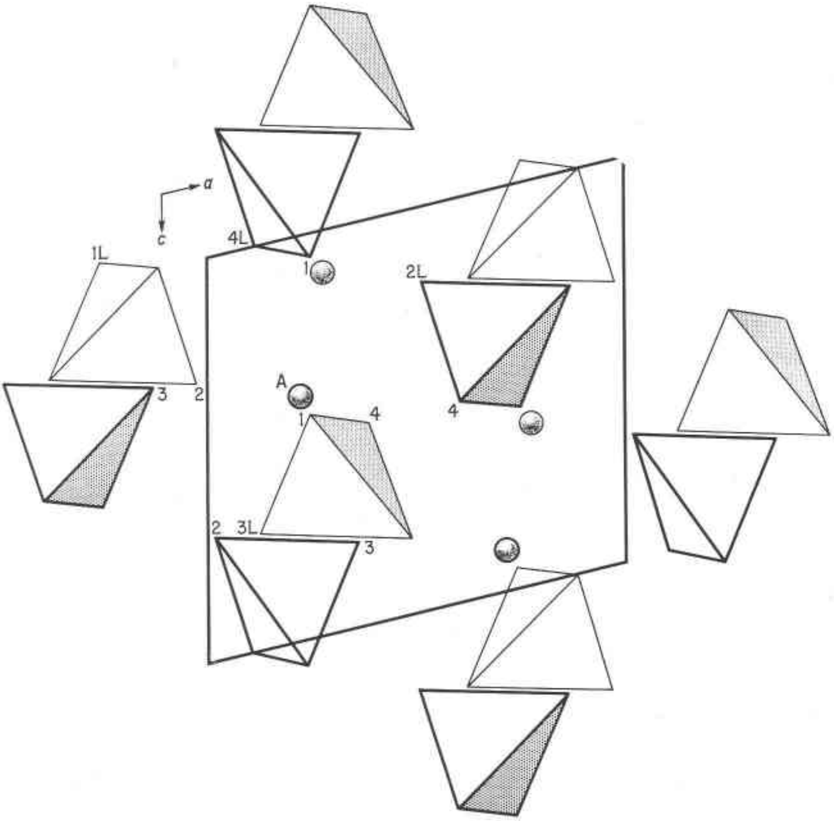

FIG. 1. View Along *b* of the Cheralite Structure. Stippled circles represent "cerium" atoms. "Cerium" (A) is bonded to numbered oxygen atoms located at corners of phosphate tertrahedra. Letter (L) following a number indicates long Ce—O bond.

The present investigation of the cheralite structure confirms the model given by Ueda (1953), Mooney (1948) and Quareni and Di Pieri (1965) for crocoite. Ghouse's (1965) structure appears incorrect. Ghouse based his structure determination upon the solution of the two orthogonal projections. This is unfortunate because it results in an ambiguity in the choice of heavy atom positions. The ambiguity can be resolved only by solution of the unique monoclinic projection along the *b* axis or by interpretation of the three-dimensional Patterson maps. We carried out a refinement of Ghouse's structure using our data, running several least-squares cycles to test convergence. The two orthogonal sets of data, the 0*kl* and *hk*0 data, refined to an acceptable degree but the *hkl* data did not refine.

TABLE 3. BOND LENGTHS AND ANGLES FOR CHERALITE.

Ce—O(1)	2.418 Å	P—O(1)	1.529 Å
	2.498	P—O(2)	1.544
	3.945	P—O(3)	1.527
		P—O(4)	1.564
Ce—O(2)	2.429		
	2.564	Average	1.541
	3.154		
		σP—O = ±0.025 Å	
Ce—O(3)	2.403		
	2.517	O(1)—P—O(2)	114.2°
	3.764	O(1)—P—O(3)	113.5°
		O(1)—P—O(4)	104.8°
Ce—O(4)	2.539	O(2)—P—O(3)	104.4°
	2.555	O(2)—P—O(4)	106.9°
	2.778	O(3)—P—O(4)	113.1°
σCe—O = ±0.025 Å		Average	109.5°

DISCUSSION

Figure 1 represents the structure of monazite minerals in general and cheralite in particular. Each phosphorus atom (not shown on the figure) is surrounded by four oxygen atoms in tetrahedral coordination at an average distance of 1.541 Å from the phosphorus (Table 3). The tetrahedron is nearly regular with respect to bond lengths but the bond angles O—PO—O range from 104.8° to 114.2°.

"Cerium" is bonded to two each of the four oxygen atoms at distances ranging from 2.403 to 2.564 Å. Longer Ce—O bonds occur with distances ranging from 2.778 to 3.945 Å (Table 3).

Each oxygen atom is bonded to three cerium atoms. Two of these bonds are short bonds and one is significantly longer. In addition, each oxygen atom is bonded to one phosphorus atom. The coordination around each oxygen atom is therefore four-fold. However, the ionic charge of each

TABLE 4. RELATIONSHIP BETWEEN LONG Ce—O, SHORT Ce—O AND P—O BONDS

O(x)	Long Ce—O	Short Ce—O[1]	P—O
1	3.945 Å	2.458 Å	1.529 Å
3	3.764	2.460	1.527
2	3.154	2.496	1.544
4	2.778	2.547	1.564

[1] Represents the mean of the two shorter Ce—O bonds.

oxygen atom is satisfied by two contributions from Ce, assuming each at +3/8, and one from P assuming that at +5/4. Although there is an apparent relationship between increase of the long Ce—O bond and decrease of the average short Ce—O bonds and the P—O bond (Table 4), the significance of this effect cannot be readily assessed with a purely ionic model.

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