

# BADDELEYITE FROM PHALABORWA, EASTERN TRANSVAAL<sup>1</sup>

S. A. HIEMSTRA, *Geological Survey, Pretoria, South Africa.*

## ABSTRACT

The rare mineral baddeleyite occurs at Phalaborwa<sup>2</sup> in the Eastern Transvaal. It has a density of  $D_{25}^{25} = 5.739 \pm 0.005$ . The optical properties are:

$$\alpha = 2.136 \pm 0.005$$

$$\beta = 2.236 \pm 0.008$$

$$\gamma = 2.243 \pm 0.008$$

$$2V_{\alpha} = 30^{\circ} \pm \frac{1}{2}^{\circ}$$

$$X \wedge c = 13^{\circ}$$

An x-ray diffraction pattern and a chemical analysis are given.

## INTRODUCTION

Baddeleyite (natural zirconia) was identified among the heavy minerals in a radioactive talus sample submitted to the author for examination by Dr. D. J. Simpson of the Geological Unit, Atomic Energy Board, in August, 1952. The associated minerals were large lumps of magnetite, notable amounts of apatite and small quantities of diopside and phlogopite. Zircon, uranoan thorianite and baddeleyite were minor constituents.

In the field the radioactivity was traced to carbonatite rocks<sup>3</sup> by the geological unit of the Atomic Energy Board. The carbonatites are composed of large irregular fragments of magnetite, calcite, yellowish chondrodite and apatite, with smaller amounts of phlogopite, chalcocite,<sup>4</sup> chalcopyrite and thorianite. Baddeleyite is a minor constituent.

## PREVIOUS WORK

L. Fletcher<sup>5</sup> published a description of a single broken crystal of baddeleyite from Ceylon. A crystallographic description in which he established the monoclinic symmetry is followed by a few optical observations on thin splinters of the mineral. Interference figures showed him the presence of inclined dispersion. His data are as follows on page 276.

<sup>1</sup> Published with the consent of the Department of Mines, and the Atomic Energy Board.

<sup>2</sup> This is the spelling of Palabora, recently adopted in the Union of South Africa.

<sup>3</sup> That these calcite-rich rocks are carbonatites was largely established from field relationships by Mr. H. D. Russell who undertook detailed mapping of the area.

<sup>4</sup> The chalcocite and chalcopyrite in this rock were identified by Mr. D. Groeneveld of this office. (Unpublished report)

<sup>5</sup> Fletcher, L., *Mineral. Mag.*, **10**, 148 (1893).

$$X \wedge c = 13^\circ$$

$$\text{Apparent axial angle} = 70^\circ - 75^\circ$$

$X$  is yellow;  $Y$  is green.

Absorption  $X > Y > Z$

$$D = 6.025$$

Blake and Smith<sup>6</sup> published their crystallographical measurements of two crystals in 1907. They found specific gravities of 5.72, 5.73 and 5.82 on three different crystals.

The last crystal (specific gravity 5.82) was used by Kathleen Yardley<sup>7</sup> in her determination of the dimensions of the unit cell, viz:  $a=5.21$ ;  $b=5.26$ ;  $c=5.375$ ;  $\beta=80^\circ 32'$ . She found that, by assuming a molecular weight of 128 for this crystal (pure zirconia 123.22), a better agreement between calculated and determined spacings was obtained. The heavier impurity could be hafnia.

Using the intensities of the  $x$ -ray reflections reported by Yardley, Náray-Szabó<sup>8</sup> was able to deduce the coordinates of the ions in baddeleyite.

Larsen and Berman<sup>9</sup> reported refractive indices of 2.13, 2.20 and 2.19 for  $\alpha$ ,  $\gamma$  and  $\beta$  respectively, an axial angle of  $30^\circ$ , and rather strong dispersion with  $r > v$ .

The various publications of Hussak, and Hussak and Reitingger were not available to the author.

#### HABIT

The baddeleyite from Phalaborwa occurs typically in the form of short black prismatic crystals, mostly between 0.05 and 1 mm. in their longest dimensions. The crystals are usually flattened parallel to  $\{100\}$ , and in addition show faces of  $\{110\}$  and  $\{011\}$ . Untwinned crystals are rare. Vertical striae caused by polysynthetic twinning with  $\{001\}$  as the composition plane can usually be seen on faces in the  $[001]$  zone, particularly on the prism faces (Fig. 1).

In thin sections cleavages were observed parallel to  $\{001\}$  and  $\{010\}$ .

#### DENSITY

Pycnometers of suitable size were not available. An acceptable accuracy could be obtained by the following method however.

The bottom of a small test tube, fitted with a notch from which it could be suspended vertically on a chemical balance, was used. It was weighed

<sup>6</sup> Blake, G. S., and Smith, H. G. F., *Mineral. Mag.*, **14**, 378 (1907).

<sup>7</sup> Yardley, K., *Mineral. Mag.*, **21**, 169 (1928).

<sup>8</sup> Náray-Szabó, St. v., *Zeit. Krist.*, **94**, 414 (1936).

<sup>9</sup> Larsen, E. S., and Berman, H., *U. S. Dept. of the Interior, Bull.* **848**, 210 (1934).

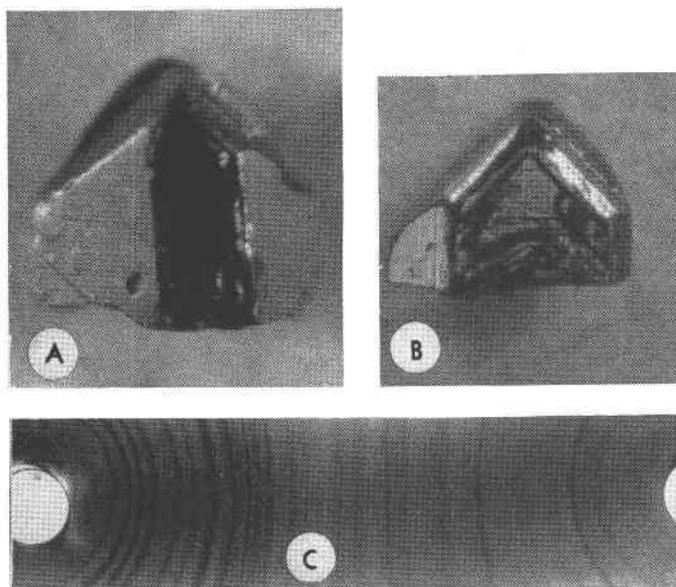


FIG. 1. *A.* Untwinned crystal of baddeleyite. ( $\times 40$ ) *B.* Twinned crystal of baddeleyite, showing vertical striae on the prism and orthopinocoid faces. ( $\times 40$ ). *C.* X-ray diffraction pattern of baddeleyite. Unfiltered Cu-radiation. 1 mm. =  $1^\circ \theta$ .

when dry, and also when suspended by means of a hair in boiled distilled water of known temperature. A small quantity of pure cleaned baddeleyite crystals (usually between 2 and 5 gm.) was introduced into the dried tube, and the tube with crystals weighed again when dry, and when suspended in boiled distilled water. Weighing after drying showed that no material was lost during the above process.

It was found to be essential however to remove all air bubbles before weighing in water. This could be done by boiling while the pressure was diminished by means of an air suction pump.

Corrections were applied for the air displaced by the weights, and for the density of the distilled water at the temperatures where observations were made.

Three determinations on different portions of material at different times gave values of 5.740, 5.737 and 5.739. The finally adopted value is:

$$D_{25}^{\text{25}} = 5.739 \pm 0.005.$$

#### OPTICAL PROPERTIES

Yellow phosphorus was used as an immersion medium for the determination of the refractive indices. After melting under water mounts

could be made with clear phosphorus which usually remained fluid in an undercooled condition for a minute or two in which the necessary observations had to be made. As determined in a prism on a one-circle goniometer, the refractive index of liquid phosphorus varies from 2.07 for red light to 2.17 for violet light (2.085 for sodium light at 25° C., the room temperature). During crystallization to an isotropic mass, the index increased to 2.12 for red light, and 2.22 for violet light (2.139 for sodium light at room temperature).

Using a monochromator,  $\alpha$  could be matched with the index of undercooled phosphorus by changing the wave-length. It is considered that the error in the value of 2.136 so obtained is of the order of 0.005.

When using solid phosphorus, a clear Becke line could not be obtained and no accurate determinations were possible. It could be established however that  $\beta$  and  $\gamma$  are both higher than the highest values attainable in solid phosphorus, namely 2.22.

Knowing  $\alpha$  fairly accurately, it only remained to determine two of the main double refractions so as to calculate  $\beta$  and  $\gamma$ .

Utilizing small crystals, orientated sections were cut in such a way that Z and X, or Z and Y were in the section plane. Using a Berek compensator, the relative retardation was determined in sodium light.

It was found difficult to prepare sections perpendicular to Y thin enough to enable one to turn the compensator drum to the position of compensation. Readings were therefore made on any "nth" compensation band. The retardation so determined differs from the wanted retardation by the amount  $n\lambda$ , (where  $\lambda$  = the wave-length of the light used).<sup>10</sup> It can therefore easily be calculated.

Thickness determinations by focussing on the top of the glass mount and on the top of the sections were inaccurate. The section and its glass mount were therefore ground away perpendicular to the section plane, until the exact spot where the retardation was determined came into view. They were now mounted on a microscope with the newly ground surface parallel to the microscope stage. Using a graduated ocular and high power objective, the thickness could be measured directly. The retardation divided by the thickness gave the amount of the double refractions ( $\gamma - \alpha$ ) and ( $\gamma - \beta$ ) equal to 0.100 and 0.007, respectively. The error in these values is thought to be less than 0.003.

The axial angle was measured on the universal stage which was fitted with glass hemispheres of high refractive index to decrease the difference between measured and true angles. The corrected value of 30° so ob-

<sup>10</sup> Burri, C., *Das Polarisationsmikroskop*, E. Birkhäuser & Cie., AG., Basel, (1950), p. 143.

tained could be duplicated to within  $\frac{1}{2}^\circ$  by repeated measurements. The value of  $28^\circ$  calculated from the refractive indices is in better agreement than could be expected from the errors assumed in the determination of  $\alpha$ ,  $\beta$  and  $\gamma$ .

Measuring the axial angle in light having wave-lengths equal to the Fraunhofer lines *F*, *D* and *C*, revealed that the amount of dispersion is less than the experimental error. A slightly smaller mean value ( $29\frac{3}{4}^\circ$ ) was obtained in blue light however. This indicates that  $r > v$ , to the extent of roughly  $\frac{1}{2}^\circ$ .

The angle between *X* and *c* was measured in a section of a twinned crystal cut parallel to {010}. The angle between the position of extinction and the composition planes increased from  $12.6^\circ$  to  $13.0^\circ$  for the Fraunhofer lines *F* and *C*, respectively.

To summarize, the optical properties are as follows:

<i>Refractive indices</i>	<i>Pleochroism</i>
$\alpha = 2.136 \pm 0.005$	<i>X</i> = dark brown
$\beta = 2.236 \pm 0.008$	<i>Y</i> = brown
$\gamma = 2.243 \pm 0.008$	<i>Z</i> = light brown
<i>Orientation</i>	<i>Axial angle</i>
$X \wedge c = 12.6^\circ (F)$	$2V_\alpha = 30^\circ \pm \frac{1}{2}^\circ$ (measured)
$X \wedge c = 12.8^\circ (D)$	
$X \wedge c = 13.0^\circ (C)$	$2V_\alpha = 28^\circ$ (calculated)
<i>Y</i> = <i>b</i>	$r > v$

The values for  $\beta$  and  $\gamma$  are considerably higher than those determined by Larsen<sup>9</sup>. His values, however, are not in good agreement with his axial angle of  $30^\circ$ .

#### CHEMICAL ANALYSIS

About 5 gm. of carefully handpicked material was submitted for quantitative chemical analysis. No other minerals were detected under the microscope, but small inclusions were possibly present. The elements found in addition to zirconium (Table 1) are all major constituents of the minerals associated with the baddeleyite, excepting titanium and manganese. Small amounts of  $\text{Fe}^3$  have been reported as substituting for  $\text{Zr}^4$  in baddeleyite.<sup>11</sup> Comparing the ionic radii of  $\text{Fe}^3$  (0.64) and  $\text{Ti}^4$  (0.68) with that of  $\text{Zr}^4$  (0.79),<sup>12</sup> it can be seen that the differences are appreciable.  $\text{Ti}^4$  will probably enter the crystal lattice more readily than  $\text{Fe}^3$ , be-

<sup>11</sup> Hevesy and Jantzen, *Zeit. anorg. Chem.*, **136**, 387 (1924), as mentioned by Palache, C., Berman, H., and Frondel, C., in Dana's System of Mineralogy, 7th. edition, Vol. 1, p. 609.

<sup>12</sup> The values for the ionic radii were taken from Green, *J. Bull. Geol. Soc. Am.*, **64**, 1001-1012 (1953).

TABLE 1. CHEMICAL ANALYSIS OF BADDELEYITE FROM PHALABORWA  
(Abraham Kruger, *Analyst*)

	Per Cent
ZrO <sub>2</sub>	95.20
SiO <sub>2</sub>	0.06
Fe <sub>2</sub> O <sub>3</sub>	2.10
MgO	0.64
CaO	0.80
MnO	0.23
TiO <sub>2</sub>	1.65
Ignition lost	0.00
Total	100.68

cause of its slightly larger radius, and also because its valence is the same as that of Zr<sup>4</sup>. The radius of Mn<sup>2</sup> (0.80) is close to that of Zr<sup>4</sup>.

Using the cell dimensions reported by Yardley,<sup>7</sup> the density determined by the writer, and a value of  $6.0597 \times 10^{23}$  for Avogadro's number,<sup>13</sup> the molecular weight of the baddeleyite was calculated and found to be 126. (Pure zirconia, 123.22.) If this calculated value is correct, then an appreciable amount of what was represented as ZrO<sub>2</sub> in the analysis actually consists of HfO<sub>2</sub>. (Mol. weight 210.6.) Assuming that the determined amounts of the lighter molecules Fe<sub>2</sub>O<sub>3</sub>, MgO, MnO and TiO<sub>2</sub> are present within the baddeleyite molecule, then the highest amount of HfO<sub>2</sub> that can be present, is 10%. If smaller amounts of the lighter molecules are present in the crystal lattice, then a correspondingly smaller amount of hafnia is necessary for a molecular weight of 126.

#### X-RAY DIFFRACTION PATTERNS

X-ray powder diffraction photographs were taken in cameras having diameters of 114.7 mm. and 57.3 mm. The films were mounted according to the method of Ievens and Straumanis. Unfiltered copper radiation produced at 35 K.V. and 20 ma. was used. A large number of lines, most of them of low intensity, and somewhat diffuse, was obtained (Fig. 1). Corrections were applied for the shrinkage of the film.

In Table 2 the *d*-values obtained by the author are compared with those reported by Yardley. No other set of values is known to the author.

#### ACKNOWLEDGMENTS

The writer is grateful to Dr. B. Wasserstein who reviewed the manuscript, and to Dr. D. J. Simpson for the material from which the mineral was obtained.

<sup>13</sup> Schlecht, W. G., *Am. Mineral.*, **29**, 108 (1944).

*Manuscript received April 20, 1954.*

TABLE 2. COMPARISON OF DIFFRACTION PATTERNS OF BADDELEYITE

Hiemstra		Yardley		
<i>Intensity</i> (Estimated)	<i>d.</i> (Å)	<i>Intensity</i>	<i>d.</i> <sup>14</sup> (Å)	<i>hkl</i>
2	5.08			
2	4.05			
4	3.66	W	3.674	011
4	3.51			
10	3.15	V.S.	3.164	11 $\bar{1}$
9	2.835	S.	2.831	111
5	2.62	M.S.	2.616	020 002
2	2.54	M.W.	2.540	200
$\frac{1}{2}$	2.44			
1	2.33	W.	2.333	012 021
3	2.21	M.	2.205	21 $\bar{1}$ 102
2	2.18			
3	2.02	M.W.	2.006	112 20 $\bar{2}$ 211
2	1.990			
4	1.847	M.S.	1.849	022
5	1.817	M.S.	1.810	21 $\bar{2}$ 220 12 $\bar{2}$
1	1.779			
2	1.688	M.	1.693	30 $\bar{1}$ 300 202
3	1.652	M.	1.658	221 013 11 $\bar{3}$
1	1.639			
1	1.609	V.W.	1.610	31 $\bar{1}$ 310
1	1.589			
3	1.541	M.W.	1.540	30 $\bar{2}$ 131
1	1.506	W.	1.510	113
1	1.498			
2	1.476	W.	1.474	311
$\frac{1}{2}$	1.447	V.W.	1.450	023
2	1.420			
$\frac{1}{2}$	1.360			
2	1.324			
2	1.263			
$\frac{1}{2}$	1.247			
$\frac{1}{2}$	1.228			
1	1.212			
1	1.177			
1	1.166			
1	1.160			
1	1.151			
1	1.140			
1	1.139			

Hiemstra		Yardley		
<i>Intensity</i> (Estimated)	<i>d.</i> (Å)	<i>Intensity</i>	<i>d.</i> <sup>14</sup> (Å)	<i>hkl</i>
1	1.115			
1	1.105			
1	1.091			
1	1.054			
1	1.044			
2	1.036			
1	1.011			
1	0.9995			
1	0.9952			
1	0.9810			
1	0.9618			
1	0.9458			
1	0.9369			
1	0.9291			
$\frac{1}{4}$	0.9226			
$\frac{1}{2}$	0.9046			
$\frac{1}{2}$	0.8981			
3	0.8859			
$\frac{1}{2}$	0.8777			
$\frac{1}{4}$	0.8688			
$\frac{1}{4}$	0.8626			
$\frac{1}{2}$	0.8552			
1	0.8465			
$\frac{1}{2}$	0.8360			
$\frac{1}{2}$	0.8293			
$\frac{1}{2}$	0.8236			
$\frac{1}{4}$	0.8184			
$\frac{1}{5}$	0.8129			
4	0.8059			
1	0.8037			
$\frac{1}{2}$	0.8007			
$\frac{1}{2}$	0.7994			
$\frac{1}{2}$	0.7937			
$\frac{1}{2}$	0.7918			
$\frac{1}{2}$	0.7776			
$\frac{1}{4}$	0.7755			

<sup>14</sup> These values were converted from Siegbahn units to Ångstroms by the writer.