PROPERTIES AND CHEMICAL FORMULA OF FOURMARIERITE

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ABSTRACT

A comparison of the optical properties of fourmarierite and becquerelite shows a similarity. This, combined with x-ray analysis, is used to deduce the chemical formula of fourmarierite.

Fourmarierite, a very rare uranium mineral, was first studied by Buttgenbach (1), who described it as orthorhombic with $a:b:c=0.883_{17}:1:0.811_5$ and specific gravity 6.046.

The chemical analysis of the mineral was made by Mélon (2). However, the sample used contained not only fourmarierite, but also some kasolite and chalcolite. From his results, Mélon concluded that the formula of fourmarierite should be $PbO \cdot 5UO_3 \cdot 10\ H_2O$. Later Schoep (3) made a new analysis which led him to the composition $PbO \cdot 4UO_3 \cdot 5H_2O$.

The optical properties deduced from Buttgenbach's and Schoep's descriptions and from measurements by Billiet, may be represented as $n_\alpha = 1.85$ along a axis, $n_\beta = 1.92$ along c, $n_\gamma = 1.94$ along b axis. Optically it is negative. Examined in convergent light with an immersion objective, a (100) cleavage lamella shows the poles of the optic axes at the edges of the field.

The absolute dimensions of the unit cell have been determined by Brasseur (5) who found $a = 14.52\ kX$, $b = 16.72\ kX$, $c = 14.07\ kX$, and pointed out that, assuming Buttgenbach's specific gravity value to be correct, the number of the molecules in the unit cell would be either 8.62 (from Schoep's formula) or 6.82 (from Mélon's formula).

Later Brasseur (6), comparing the optical properties of fourmarierite and becquerelite, suggested a possibility of checking the value of M/ρ (M, molecular weight; ρ, density). Although it was possible definitely to reject Mélon's formula, two erroneous facts led to a conclusion which should be corrected: First, the refractive indices used for becquerelite were those given by Billiet; it has been shown since that these values were incorrect and that the actual indices are:

n_α, 1.725 or $n_\alpha = 1.735$	1.730	$n_\beta = 1.825$ / $n_\beta = 1.820$	1.822_5	$n_\gamma = 1.830$ / $n_\gamma = 1.830$	Schoep & Stradiot (7), Larsen (8).

Second, the specific gravity had been measured on poor crystals. Under the circumstances, it was decided to re-examine the formula of fourmarierite, taking new data into account.

Thanks to a gift from the "Union minière du Haut Katanga", it was possible to select 15 to 20 mg. of very pure fourmarierite. Using Berman's microbalance, the specific gravity was found to be (at 21° C.) $\rho = 5.755$, $\rho = 5.689$, $\rho = 5.777$. The mean of these values, 5.740 ± 0.051 (21° C.), should be the best value of the density ever given for fourmarierite.

New measurements were also made, by the same method, of the specific gravity of highly pure becquerelite of the same origin. The results obtained, $\rho = 5.125$, $\rho = 5.056$, $\rho = 5.090$, lead to a mean value 5.090 ± 0.035 (21° C.).

Measurements of the refractive indices of becquerelite were made by the prism method $(00\bar{1}):(101)$ in order to confirm the figures given by Schoep and Stradiot, and by Larsen. Three different prisms were used.

Goniometric Angle	Prism Angle	Index parallel to b		Index perpendicular to b	
		578 mμ	541 mμ	578 mμ	541 mμ
132°47′	47°13′	1.816	1.840	1.792	1.809
132°50′	47°10′	1.826	1.840	1.805	1.811
133°15′	46°45′	1.823	1.837	1.798	1.812
Mean Values		$1.82_2 \pm 0.006$	$1.83_9 \pm 0.002$	$1.79_8 \pm 0.007$	$1.81_1 \pm 0.002$

Values obtained for the index n_β parallel to b (for $\lambda = 578$ mμ) are seen to be in good agreement with those published by Schoep and Stradiot, and by Larsen. As to the values obtained for the index perpendicular to b, they give only a check for the accuracy of the measurements of n_α and n_γ and agree better with $n_\alpha = 1.735$.

In order to make the calculations possible, it was necessary to redetermine the formula of becquerelite, taking into account the new value of the specific gravity. The dimensions of the unit cell of becquerelite had been previously determined by Billiet and de Jong (9), who found for this orthorhombic mineral: $a = 13.9$ kX, $b = 12.55$ kX, $c = 14.9$ kX. Our values differ from these by an amount smaller than the experimental error ($\cong 0.5\%$). Accordingly, calculations can be made using these figures. Three formulas have been proposed: $2UO_3 \cdot 3H_2O$ (I), $3UO_3 \cdot 5H_2O$ (II), $UO_3 \cdot 2H_2O$ (III). Formula I leads to 12.81 (i.e. 12+6.75%) molecules per cell; formula II leads to 8.46 (i.e. 8+5.75%) molecules per cell; formula III leads to 24.90 (i.e. 24+3.75%) molecules per cell. The space group being V_h^{16}, the cell cannot contain either 13 or 25 molecules. There seems to be little doubt that the real formula is nearer $UO_3 \cdot 2H_2O$ than either of the other two.

Using this formula and assuming the coordination of oxygen round the uranium atom to be the same in becquerelite and fourmarierite, calculations lead to the following refractivities. From becquerelite, $I_{UO_3-\beta \simeq \gamma} = 20.4$

and $I_{UO_3-\alpha}=18.0_3$. These values have been used for the following calculations (see (6)), in which $R\rho/M=(n^2-1)/(n^2+2)$, where R is the molecular refractivity; M, the molecular weight; ρ, the density; and n, the refractive index.

Formula	$R_{\beta\cong\gamma}$	M	$\frac{R}{M}$	ρ	$\frac{R}{M}\rho$	$n_{\beta\cong\gamma}$	R_α	$\frac{n_\alpha^2-1}{n_\alpha^2+2}$	n_α
$PbO\cdot 4UO_3\cdot 5H_2O$	112.43	1457	.0772	5.63	.435	1.82			
$PbO\cdot 4UO_3\cdot 6H_2O$	116.49	1475	.0789	5.70	.450	1.86			
$PbO\cdot 4UO_3\cdot 7H_2O$	120.55	1493	.0806	5.77	.465	1.90	110.95	.429	1.805
$PbO\cdot 4UO_3\cdot 8H_2O$	124.61	1511	.0823	5.84	.481	1.94_5	115.01	.444	1.840
$PbO\cdot 4UO_3\cdot 9H_2O$	128.67	1529	.0841	5.91	$.497_5$	1.99			

It can be seen, from these results, that the most probable formula for fourmarierite should be either $PbO\cdot 4UO_3\cdot 7H_2O$ or $PbO\cdot 4UO_3\cdot 8H_2O$. The first one is in good agreement with the measured density but leads to somewhat low values for the indices; the second one is in good agreement with the values of the refractive indices, but gives too high a value for the density.

Whether the formula of fourmarierite should be $PbO\cdot 4UO_3\cdot 7H_2O$ or $PbO\cdot 4UO_3\cdot 8H_2O$ cannot be decided from the foregoing results. However, it may be noticed that there is a close similarity between becquerelite and fourmarierite. Both are orthorhombic, optically negative, and the dimensions of the unit cell are, respectively, $a=13.9$ *kX*, $b=12.55$ *kX*, $c=14.9$ *kX* for becquerelite, $a=14.5$ *kX*, $b=16.7$ *kX*, $c=14.07$ *kX* for fourmarierite. This suggests the possibility that the number of oxygen atoms in fourmarierite be 4/3 of the number of oxygen atoms in becquerelite. As the number of oxygen atoms in becquerelite is 120, the corresponding number in fourmarierite would be 160, which points to the formula $PbO\cdot 4UO_3\cdot 7H_2O$.

In conclusion, I would like to express my thanks to the Union minière du Haut Katanga for providing the necessary fourmarierite and becquerelite samples.

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