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The Crystal Structure of Ytterbium Diiodide Monohydrate by X-Ray Powder Diffraction

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The crystal structure of the ytterbium diiodide monohydrate was determined by the X-ray powder diffraction method. Ytterbium atoms are octahedrally coordinated by five iodine atoms and one oxygen atom; space group: *Pnma* (62); lattice parameters: a = 10.4792(7), b = 4.5138(3), c = 13.0602(9) Å. Rietveld refinement of a mixture of ytterbium diiodide hydrate and a silicon standard results in the discrepancy factors R_B = 8.04, R_{wp} = 9.17%. The powder pattern previously reported for $YbI_2 \cdot 2H_2O$ is shown to be identical to that of $YbI_2 \cdot H_2O$.

INTRODUCTION

Two ytterbium diiodide hydrates have been reported previously (1). One of them, described as a "dihydrate," can be detected in many experiments where YbI_2 is used as a reagent. Further hydration of this "dihydrate" is very rapid and results in higher hydrates which have not been yet fully characterized (1, 2). The crystal structure determination of this common hydrate is the subject of this paper. Because numerous attempts to prepare a single crystal of this compound were unsuccessful, the structure determination was undertaken from powder diffraction data. These results represent the first structure determination of a divalent rare-earth iodide hydrate.

EXPERIMENTAL

The ytterbium diiodide hydrate was prepared strictly according to the published procedure (1). Reaction of YbI_2 with $CuSO_4 \cdot 5H_2O$ was carried out at 5°C; reaction time was 14 days. Since ytterbium iodide hydrates are very moisture and oxygen sensitive, the X-ray diffraction pattern was obtained in an evacuated Guinier camera with monochromatized Cu$K\alpha_1$ radiation. The purity of the reagents and obtained compounds was verified by X-ray diffraction; NBS certified Si (a = 5.430821(3) Å) was used as an internal standard in all X-ray diffraction experiments. The pattern could be indexed with orthorhombic lattice parameters that corresponded exactly to those reported by Kim *et al.* (1), for $YbI_2 \cdot 2H_2O$. The structure determination and refinement was based on one Guinier film which was digitized on a computer-controlled film scanner to obtain a set of Y_{obs}. Measured intensities were corrected for a nonlinearity of the film sensitivity (3). Integrated intensities were corrected by the LP factor typical of the Guinier method and plane multiplicity factors (4).

STRUCTURE DETERMINATION

Integrated intensities of 31 nonoverlapping reflections were used to determine the structure. Because the number of reflections was small, three space groups were considered: *Pnma*, *Pbma*, and *Pcma*. A promising solution was found only in space group *Pnma*. A Yb and one I atom were found initially by the automatic Patterson analysis procedure of the SHELXS-86 program (5). After refinement of these Yb and I positions using the SHELX-76 program (6), the other I atom was located by Fourier methods. Next, the heavy atom positions were refined by the Rietveld refinement program DBWS 9006PC (7). The Rietveld refinement was performed for a mixture of the ytterbium diiodide hydrate and the silicon standard. The structure factors of the YbI_2 hydrate evaluated by this program were used in the input file to SHELX-76 and difference Fourier maps were calculated again. Only one oxygen atom was found by the Fourier methods; there were no additional pronounced electron density maxima at a reasonable distance from other atoms. Rietveld and Fourier map calculations were also performed using the same data set and programs of the XRS-82 (8) system; the results obtained are essentially the same.

STRUCTURE DESCRIPTION

Details of the refinement procedure are presented in Table 1. Atomic positions and interatomic distances are given in Tables 2 and 3, respectively. The monohydrate is a layered compound with all atoms in the special 4c position of space group *Pnma*. Ytterbium atoms are octahedrally coordinated by five iodine atoms and one oxygen atom. The coordination number of the ytterbium cations

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TABLE 1
Crystallographic and Rietveld Refinement Data for YbI_2 Monohydrate

Pattern range 2Θ	10.–72.0
Step size 2Θ	0.02475[a]
Wavelength Cu$K\alpha_1$ (Å)	1.54056
Space group	*Pnma* (62)
a (Å)	10.4792(7)
b (Å)	4.5138(3)
c (Å)	13.0602(9)
Volume (Å^3)	617.8(1)
Z	4
Number of observations	2506
Number of contributing reflections	174
Number of refined structural parameters	15
Number of refined profile parameters	15
Peak shape	1 mod Lorentzian
U, V, W	0.269, −0.103, 0.025
Peak range (in HW)	4.0
$R_{wp} = 100[\Sigma\, w_i(y_i - y_{ci})^2/\Sigma\, w_i y_i^2]^{1/2}$	9.17
$R_p = 100\ \Sigma\, \lvert y_i - y_{ci}\rvert/\Sigma\, \lvert y_i\rvert$	6.69
$R_B = 100\ \Sigma\, \lvert I_o - I_c\rvert/\Sigma\, I_o$	8.04
Maximum shift to error	0.3

[a] Refined by least-squares method.

is the same as that in anhydrous YbI_2. Similar coordination is observed in calcium diiodide tetrahydrate (11) (Yb and Ca radii are almost identical (12)). Figure 1 shows the structure of $YbI_2 \cdot H_2O$ viewed down the b axis. The structure is composed of $Yb_2I_{10}O_2$ units resulting from the edge sharing of two YbI_5O octahedra related by an inversion center. These units are held together by common edges to form infinite prisms parallel to the b axis. The plot of the observed and calculated pattern is presented in Fig. 2. The lattice parameters suggest similarities of investigated YbI_2 monohydrate to other monohydrates (9, 10); e.g., all six monohydrates investigated by Lutz *et al.* (9), also crystallize in space group *Pnma*, with all atoms in the special 4c position as monohydrate described here. However, atomic positions, interatomic distances, and coordination numbers are different.

It is difficult to explain why the lattice parameters (and X-ray powder pattern) reported for $YbI_2 \cdot H_2O$ (1) should be found identical to those of one which refines as a monohydrate. However, YbI_2 hydrates are known to lose water of hydration upon evacuation (1), and it is probable that the investigated sample transforms to the monohydrate upon exposure to a vacuum during the Guinier camera experiment.

Crystal structures of other YbI_2 hydrates and the relation between the structure of anhydrous YbI_2 and its hydrates will be the subject of further investigations.

TABLE 2
Positional and Thermal Parameters for YbI_2 Monohydrate

Atom	x	y	z	B
Yb	0.1907(3)	0.25	−0.0311(3)	3.2(1)
I(1)	−0.0285(4)	0.25	0.1441(3)	4.2(1)
I(2)	0.3347(4)	0.75	0.0871(3)	4.8(2)
O	0.3357(38)	0.25	−0.172(26)	8.3(1.6)

TABLE 3
Comparison of Selected Interatomic Distances in $YbI_2 \cdot H_2O$ and Similar Compounds[a]

$YbI_2 \cdot H_2O$		YbI_2
Yb–I 2×	3.188(4)	3.131
Yb–I 1×	3.242(5)	
Yb–I 2×	3.129(4)	
Yb–O	2.39(4)	2.245–2.288[b]
I–I	4.406(6)–4.514(4)	4.346–4.513
I–O	3.62(4)–3.87(3)	3.568–3.947[c]

[a] Data for YBI_2 (13), except as noted.
[b] Yb–O distance observed in Yb_4OCl_6 (14), the only compound containing Yb^{+2}, O^{-2}, and X^{-1} (X = halogen) found in the literature.
[c] Reference (11).

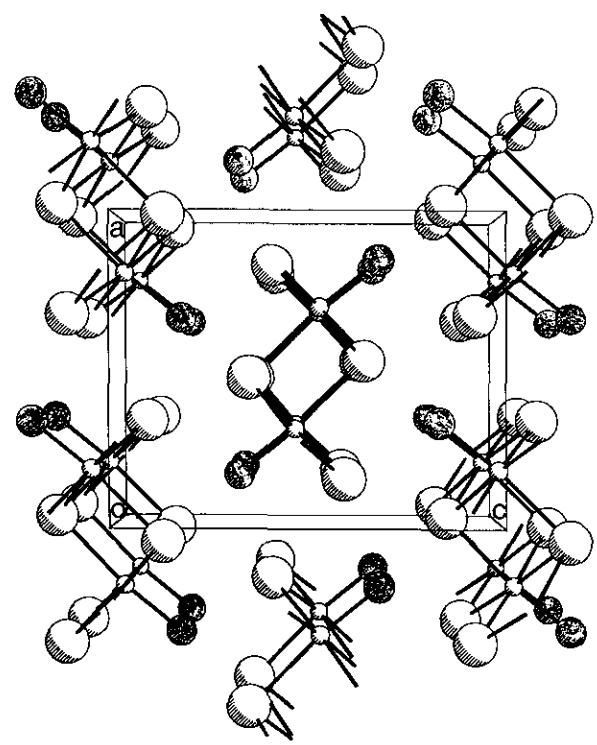

FIG. 1. Structure of $YbI_2 \cdot H_2O$ viewed down the b axis. The small and large circles represent ytterbium and iodide atoms, respectively; grey circles represent oxygen.

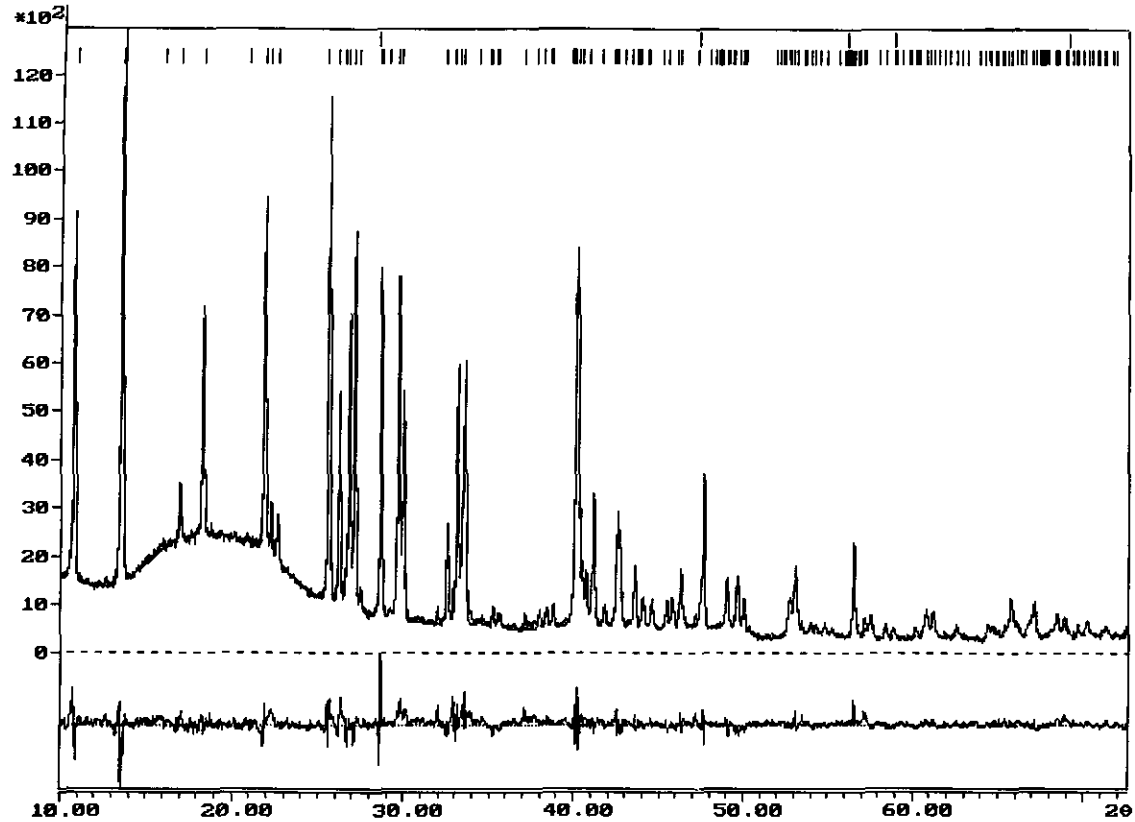

FIG. 2. Observed and calculated diffraction pattern for a mixture of $YbI_2 \cdot H_2O$ and Si with a difference plot indicated at the base of the figure. Marks at the top indicate Si and $YbI_2 \cdot H_2O$ peak locations.

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