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# The Crystal Structure of the Hydrogarnet $Ba_3In_2(OD)_{12}$

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The structure of $Ba_3In_2(OD)_{12}$ has been determined from time-of-flight neutron powder data. The structure is that of hydrogarnet, space group $Ia\bar{3}d$, $a$ = 14.0658(2) Å. Oxygen parameters are $x$ = −0.02960(9), $y$ = 0.05343(9), $z$ = 0.14041(8). Hydrogen (D) parameters are $x$ = −0.0912(1), $y$ = 0.0424(1), $z$ = 0.1567(1). The O–D bond length is 0.909 Å. Some features of hydrogarnet crystal chemistry are discussed. 

## Introduction

Hydrogarnets are cubic compounds $A_3B_2(OH)_{12}$ in which $A$ is an alkaline earth cation (Ca, Sr, or Ba) in eight-coordination and $B$ is a trivalent cation (Al, Fe, Ga, Cr, Sc, or In) in octahedral coordination. The $A$, $B$, and O atoms occupy positions similar to those in the anhydrous garnets $A_3B_2C_3O_{12}$. The $A$ and $B$ atoms are in special positions and the O and H atoms in general positions of $Ia\bar{3}d$. The prototype hydrogarnet $Ca_3Al_2(OH)_{12}$ is of considerable interest as it forms solid solutions with grossular $Ca_3Al_2Si_3O_{12}$ and such compounds may well be a major source of stored water in the earth's mantle (*1*). The substitution of $H_4$ for Si also suggests a possible way of incorporating hydrogen in silicate minerals in general (*2*).

$Ca_3Al_2(OH)_{12}$ itself has been the subject of a number of structural studies with an accurate set of results recently reported (*3*). There are several features of interest in the structure (referred to below) so that we have undertaken a structural study of another hydrogarnet to see if these features are common to hydrogarnets in general. $Ca_3Al_2(OH)_{12}$ has the smallest unit cell of known hydrogarnets ($a$ = 12.58 Å) so we decided to investigate the hydrogarnet $Ba_3In_2(OH)_{12}$ which has the largest known cell volume ($a$ = 14.07 Å).

## Synthesis

The preparation of $Ba_3In_2(OH)_{12}$ was first described by Kwestroo *et al.* (*4*), who characterized the material by qualitative X-ray powder diffraction. Their method involves the prolonged refluxing of $BaCl_2$ and $In_2O_3$ in 12 $N$ NaOH at 110°C; in our hands, this procedure produced $Ba_3In_2(OH)_{12}$ contaminated with unidentified

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minor phases. We found that very nearly pure $Ba_3In_2(OH)_{12}$ could be prepared by first preparing pure $Ba_3In_2O_6$ by prolonged reaction of stoichiometric amounts of $BaCO_3$ and $In_2O_3$ at a final temperature of 1300°C. The $Ba_3In_2O_6$ was then reacted with 12 *N* NaOD (99.5% isotopically pure) at 85°C for 12 hr under a pure nitrogen atmosphere to produce a pure sample of $Ba_3In_2(OD)_{12}$ suitable for neutron powder diffraction.

TABLE I

POSITIONAL PARAMETERS[a] FOR $Ba_3In_2(OD)_{12}$

| Atom | Position | *x* | *y* | *z* |
|---|---|---|---|---|
| Ba | 24*c* | $\frac{1}{8}$ | 0 | $\frac{1}{4}$ |
| In | 16*a* | 0 | 0 | 0 |
| O | 96*h* | −0.02960(9) | 0.05343(9) | 0.14041(8) |
| D | 96*h* | −0.0912(1) | 0.0424(1) | 0.1567(1) |

[a] Space group $Ia\bar{3}d$, $a$ = 14.0658(1) Å. Standard deviations in parentheses.

## Structure Determination

A preliminary quantitative X-ray powder diffraction study (Rigaku DMAX-II wide-angle goniometer Cu$K\alpha$ radiation) confirmed the space group ($Ia\bar{3}d$) and the metal atom positions and provided approximate oxygen atom coordinates.

Neutron data were collected on the high-resolution time-of-flight neutron powder diffractometer (NPD) at the Los Alamos Neutron Scattering Center (LANSCE). The refinement of the structure was made using data from the −148° and 90° detector banks and the Generalized Structure Analysis System (GSAS) which employs a Rietveld profile analysis (*5*). Approximate hydrogen (D) positions were readily found by a difference Fourier map using the Ba, In, and O positions. The final refinement utilized data for 1002 peaks in the range $0.5 < d < 3.0$ Å (13,003 data points). The variables refined included 12 background parameters, a scale factor, four peak profile parameters ($\alpha_1$, $\beta_0$, $\beta_1$, $\sigma_1$) (*5*), a diffractometer zero constant, atomic positional parameters for O and D and anisotropic thermal parameters. The final agreement indices are $R_p$ = 0.033 and $R_{wp}$ = 0.050 with a reduced $\chi^2$ = 1.80 for 62 variables. Figure 1 shows the final profile fit for the −148° data. Atomic structure parameters are given in Tables I and II and structure amplitudes are given in Table III.[1]

## Discussion

Selected distances and angles in $Ba_3In_2(OD)_{12}$ are presented in Table IV. The Ba–O and In–O distances are very close to the values (2.798 and 2.158 Å) expected (*6*) for bonds of valence $\frac{1}{4}$ and $\frac{1}{2}$, respectively. Structural features worthy of note include the following.

(i) In contrast to anhydrous garnets in which the two independent *A*–O bond lengths differ by typically about 5%, the two independent Ba–O distances differ by only 1%. The situation therefore resembles that in $Ca_3Al_2(OD)_{12}$ (*3*) in which the two Ca–O distances are even closer.

(ii) The short O–D distance (0.909 Å) is indicative of an absence of hydrogen bonding [contrast the O–H distance of 1.012 Å in $In(OD)_3$ (*7*) in which there is

[1] See NAPS document No. 4765 for 27 pages of supplementary material. Order from ASIS/NAPS. Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 up to 20 pages plus $0.30 for each additional page. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $4.50 for postage and handling, for the first 20 pages, $1.00 for each additional 10 pages of material, and $1.50 for postage of any microfiche orders.

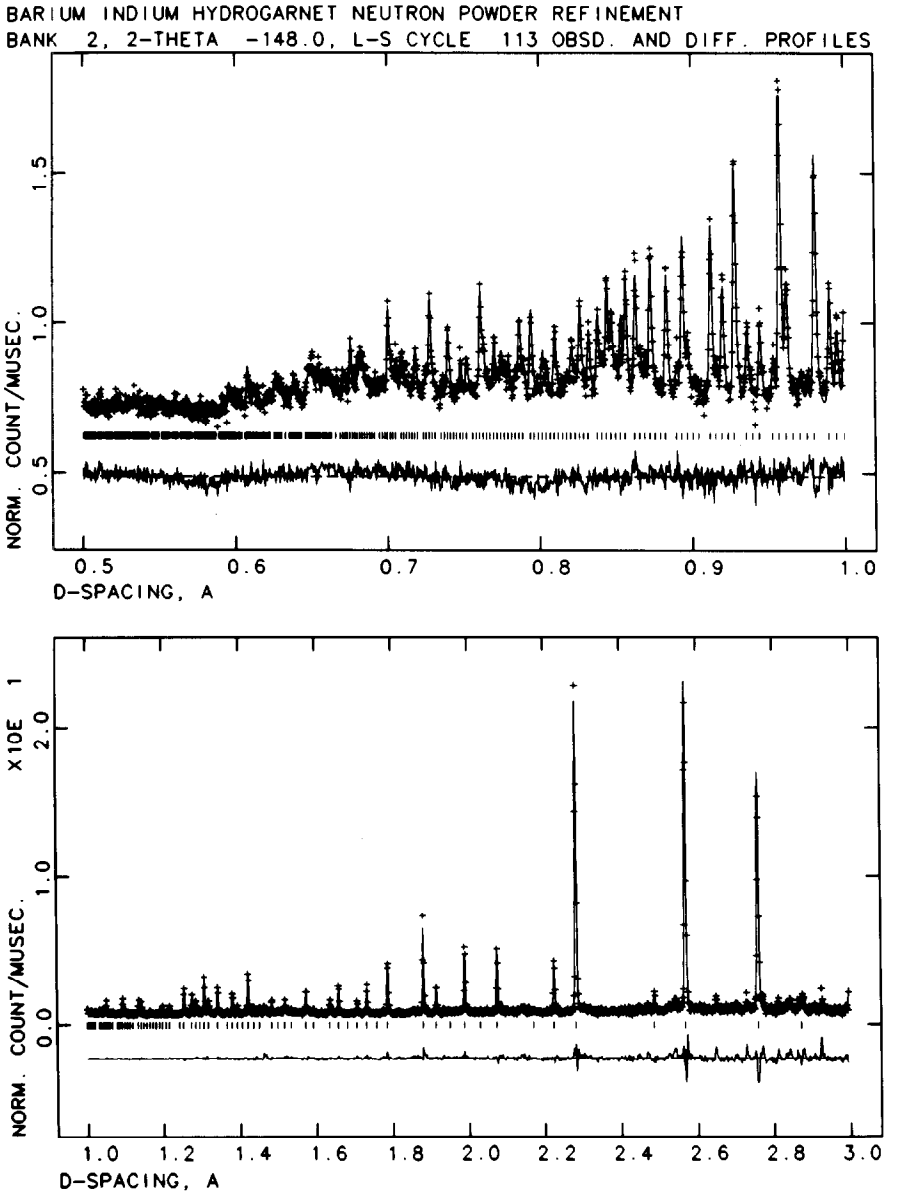


FIG. 1. Neutron profile fit for $Ba_3In_2(OD)_{12}$. The data points for the $-148°$ detector bank are shown as "+" and the calculated profile as a solid line. The tick marks below the profile indicate the position of Bragg peaks. The lower curve is the difference between observed and calculated data on the same scale as the profile, but with shifted ordinate.

TABLE II

ANISOTROPIC THERMAL PARAMETERS[a] FOR $Ba_3In_2(OD)_{12}$

| Atom | $100U_{11}$ | $100U_{22}$ | $100U_{33}$ | $100U_{12}$ | $100U_{13}$ | $100U_{23}$ |
|---|---|---|---|---|---|---|
| Ba | 2.28(14) | 1.63(7) | 1.63(7) | 0 | 0 | 0.06(7) |
| In | 1.46(6) | 1.46(6) | 1.46(6) | −0.20(7) | −0.20(7) | −0.20(7) |
| O | 2.24(7) | 2.38(7) | 2.08(6) | 0.06(5) | 0.15(5) | −0.27(5) |
| D | 4.29(10) | 9.75(15) | 5.76(11) | −1.59(9) | 2.04(8) | −2.26(9) |

[a] In Å$^2$ with standard deviations in parentheses.

TABLE IV

SELECTED DISTANCES (Å) AND ANGLES IN $Ba_3In_2(OD)_{12}$[a]

| | |
|---|---|
| Ba–O | 2.769(1) (X4) |
| | 2.805(1) (X4) |
| In–O | 2.619(2) (X6) |
| D–O | 0.909(2) |
| D–D | 2.249(2) (X2) |
| | 2.481(2) |
| In–O–D | 110.8(1) |
| Ba–O–D | 124.1(1) |

[a] Standard deviations in parentheses.

clearly hydrogen bonding]. In fact the next nearest D . . . O distance is 2.86 Å and the shortest O . . . O distance is 2.93 Å (in an edge shared between the $BaO_8$ and the $InO_6$ polyhedra). Again the situation closely resembles that of $Ca_3Al_2(OD)_{12}$ in which the O–D distance is 0.906 Å (*3*).

(iii) The general disposition of the D atoms is very similar to that in $Ca_3Al_2(OD)_{12}$. Groups of four D atoms in a flattened tetrahedron with $\bar{4}$ symmetry are centered on 24 *d* sites (occupied by *C* atoms in the anhydrous garnets $A_3B_2C_3O_{12}$). This tetrahedron interpenetrates an elongated tetrahedron of O atoms as illustrated in Fig. 2. The distances of D and O from the $\bar{4}$ site (*d*) are (with the corresponding values for $Ca_3Al_2(OD)_{12}$ in parentheses) *d*–D = 1.518 (1.342) Å; *d*–O = 2.177 (1.949) Å. It may be seen that the two $\bar{4}$ tetrahedra are considerably expanded in $Ba_3In_2(OD)_{12}$.

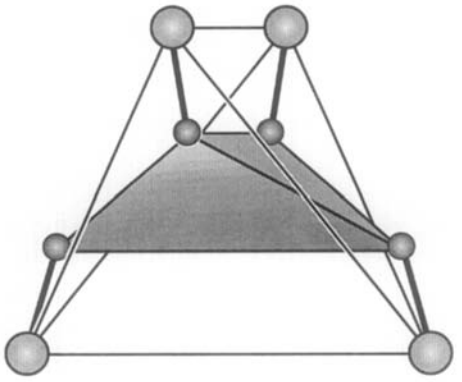

FIG. 2. The arrangement of four OD groups about a $\bar{4}$ site in $Ba_3In_2(OD)_{12}$. The $\bar{4}$ axis is vertical in the plane of the drawing. Larger circles represent O atoms, smaller circles D atoms. The "squashed" tetrahedron formed by the D atoms is shaded and the elongated tetrahedron formed by the O atoms is outlined.

The structure type raises some interesting problems for those who would model crystal structures. If it is supposed (as we consider likely) that, once the other atoms are fixed, the H atom coordinates ($x_H$, $y_H$, $z_H$) are determined by the O–H bond length and the In–O–H and Ba–O–H bond angles, there are four parameters remaining to be determined ($a$, $x_O$, $y_O$, $z_O$); however, there are only three other independent bond lengths (two Ba–O and one In–O). This situation should be compared with that in the anhydrous garnets in which there are four structural parameters and four independent bond lengths, so that a good estimate of the parameters can be derived from the expected bond lengths (*8*).

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