

The Crystal Structure of Sr(OD)₂

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The crystal structure of Sr(OD)₂ has been determined from a Reitveld refinement of time-of-flight neutron diffraction data, and the deuterium atom positions have been determined for the first time. The structure is orthorhombic: *Pnma*, $a = 9.8269(5)$ Å, $b = 3.9051(2)$ Å, $c = 6.0733(3)$ Å, $V = 233.06$ Å³, $D_x = 3.466$ g cm⁻³, $R_{wp} = 3.93\%$, $R_p = 2.95\%$, reduced $\chi^2 = 4.774$ for 81 variables. Although the data were collected at 12 K, the H atoms have large thermal parameters suggesting the possibility of some disorder. Relationships of the structure to the structures of YOOH, SrBr₂, SrI₂, and SrBr₂ · H₂O are discussed. © 1995 Academic Press, Inc.

INTRODUCTION

The structures of the alkaline earth hydroxides, in particular the hydrogen positions, O-H bond lengths, and the presence or absence of hydrogen bonding continue to be lively topics for research and discussion. These hydroxides present a wide array of structures: those of Be(OH)₂, Mg(OH)₂, Sr(OH)₂, and Ba(OH)₂ are all different. Recent work on Mg(OH)₂ (brucite) includes an accurate determination of the H positions at low pressure (1) and the effect of pressure on hydrogen positions and O ··· O distances (2). A recent study (3) of Ca(OH)₂ (portlandite) suggests that, as might have been predicted, the zero-pressure structure has features (such as disordered H atom positions) in common with high-pressure Mg(OH)₂. Although no phase transition under pressure for Mg(OH)₂ has yet been reported, it might be expected that should one occur, a strong candidate for the high-pressure structure would be that of Sr(OH)₂. As such it is of interest as a possible lower mantle mineral structure.

A partial structure for Sr(OH)₂ was reported by von Grueninger and Bärnighausen (4). In that study the hydrogen atom positions were not determined, as their data were collected using X rays. In this work a neutron powder diffraction study of Sr(OD)₂ was undertaken to determine the deuterium positions.

EXPERIMENTAL

The deuterated sample of hydrated strontium hydroxide, Sr(OD)₂ · 8D₂O, was synthesized by the addition of

D₂O to strontium metal. The hydrate was converted to the anhydrous hydroxide by heating at 120°C for several days. The composition was confirmed by thermogravimetric analysis (TGA) of the hydrated material which showed, in agreement with earlier reports (5), that all water was removed by this treatment. An X-ray diffraction pattern of the material prepared in this way corresponded to the orthorhombic cell earlier reported (4) with no indication of a second phase.

Neutron powder diffraction data were collected at 305 and 12 K on the general purpose powder diffractometer (GPPD) at the intense pulsed neutron source (IPNS) at Argonne National Laboratory. The data were collected using the ±148°, ±90°, and ±60° detector banks, which were symmetrically summed following the collection and covered a *d*-spacing range from 0.4 to 5.7 Å. There was no obvious difference between the high- and low-temperature data, so only the 12 K data were refined.

The structure was refined using the general structure analysis system (GSAS), a Rietveld profile analysis code developed by Larson and Von Dreele (6). The starting structure used the Sr and O positions reported by von Grueninger and Bärnighausen (4) and approximate positions of the deuterium atoms determined from a difference Fourier map. Systematic absences indicated symmetry *Pna** [* = *m* (centrosymmetric) or 2₁ (acentric)]; a refinement in *Pna*2₁ did not produce a significant difference from one in *Pnam* so we believe the latter to be correct and results are reported in the standard setting *Pnma*.

The structural model was refined for lattice parameters, atomic positions, and anisotropic thermal parameters in the case of the deuterium atoms. Background coefficients, scale factor, anisotropic strain terms in the profile function, and sample absorption were also refined.

The final refinement of the data used 11,463 observations for 2275 reflections; $\chi^2 = 4.8$, $R_{wp} = 3.9\%$, $R_p = 2.9\%$ for a total of 81 parameters. Examples of the data and calculated fit are shown in Fig. 1.

RESULTS AND DISCUSSION

Structural and thermal parameters are reported in Table 1. Notice the large thermal parameters associated with

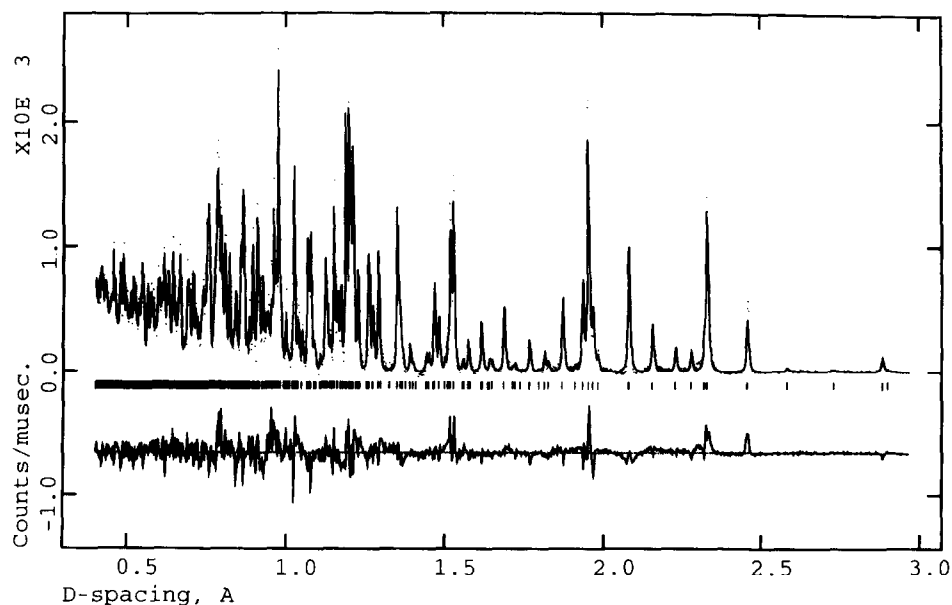


FIG. 1. TOF neutron diffraction profile fit to the summed 153° bank. The data are shown as $+$. The solid line is the calculated profile and the difference curve is shown at the bottom on the same scale.

the D atom positions (see also Fig. 2). As the structure determination was performed at 12 K, it is unlikely that the large thermal parameters truly reflect dynamic disorder and it is possible that the H atoms are disordered over several positions as in $\text{Ca}(\text{OH})_2$ (3) and in high-pressure $\text{Mg}(\text{OH})_2$ (2).

Selected interatomic distances are reported in Table 2. Also reported are bond valences and bond valence sums (7) at the individual atoms. It may be seen that Sr is seven-coordinated to oxygen. The bond valence sum at Sr is very close to the value (2.0) expected so we are confident that the Sr and O atom have been accurately located. If one takes the centroid of the "thermal" ellipsoid as the D atom positions, one obtains the O–D bond lengths re-

ported in the table. The O(2)–D(1) distance is rather short but is significantly increased for "riding" motion using the algorithm of Busing and Levy (8); however, it should be emphasized that it is possible that the D atoms have static disorder, in which case a riding-motion correction is not appropriate. The shortest O \cdots O distances in the structure are one O(1) \cdots O(2) distance of 2.96 Å; all the other O \cdots O distances are greater than 3 Å, much too large for there to be any significant hydrogen bonding (9). The shortest D \cdots D distance is D(1) \cdots D(2) = 1.91 Å.

In strontium hydroxide the strontium atoms are seven-coordinated by oxygen in a monocapped trigonal prism. The structure is closely related to that of YOOH (10, 11) in which Y has a similar coordination. In both structures

TABLE 1
Atomic Coordinates^a and Thermal Parameters^b for $\text{Sr}(\text{OD})_2$

	<i>x</i>	<i>z</i>	<i>u</i> ₁₁ or <i>u</i> _{iso}	<i>u</i> ₂₂	<i>u</i> ₃₃	<i>u</i> ₁₃
Sr	0.1587(2)	0.8968(3)	0.16(3)			
O(1)	0.3918(2)	0.6523(3)	0.02(3)			
O(2)	0.3735(2)	0.1390(3)	0.29(4)			
D(1)	0.9137(2) (0.9147)	0.6892(3) (0.6822)	4.3(1)	2.7(1)	3.7(1)	1.9(1)
D(2)	0.4558(3) (0.4599)	0.1175(4) (0.1164)	9.2(2)	1.73(9)	4.0(1)	4.5(2)

Note. Deuterium positions corrected for riding motion are shown in parentheses below noncorrected values.

^a Space group $Pnma$, $a = 9.8269(5)$ Å, $b = 3.9051(2)$ Å, and $c = 6.0733(3)$ Å, all atoms in 4 (*c*): $x, 1/4, z$.

^b Thermal parameters are to be multiplied by 10^{-2} Å.

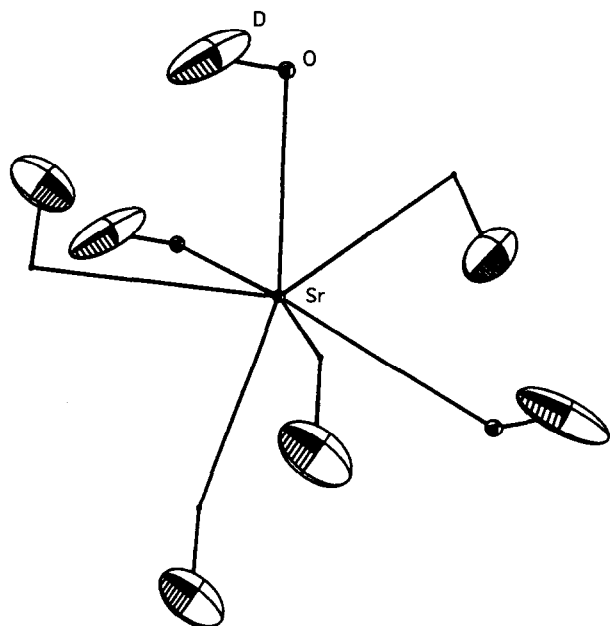


FIG. 2. ORTEP drawing of the OD groups around the central strontium atom; thermal motion is shown at 50% density. Note the large "wagging" of the deuterium atoms.

the trigonal prisms form layers with the seventh metal–oxygen bond joining the layers together as shown in Fig. 3.

Hyde and Andersson (11) remark on the relationship between the YO₂ part of the structure of YOOH and that of the SrO₂ part of SrBr₂·H₂O (12). As shown in Fig. 3 and Table 3, there is an even closer correspondence of the SrO₂ part of Sr(OH)₂ and "SrBr₂." The only significant difference is that water is intercalated between the layers of trigonal prisms in SrBr₂·H₂O. The TGA data and subsequent structural refinement preclude the possibility of our material being Sr(OD)₂·D₂O. However, they do sug-

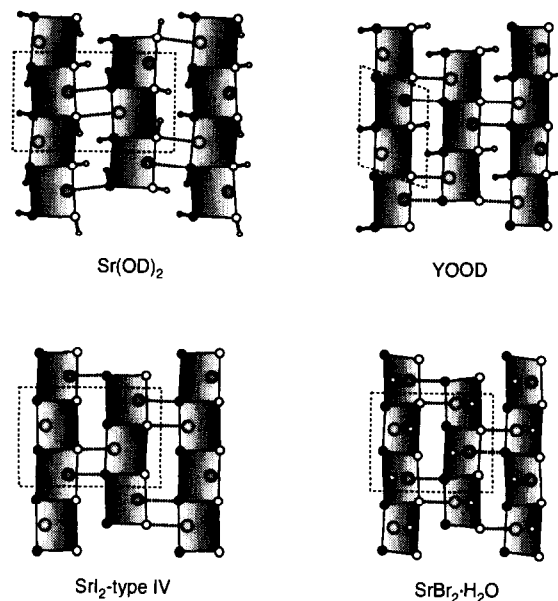


FIG. 3. Comparison of the structures of Sr(OD)₂, YOOD, form IV of SrI₂, and SrBr₂·H₂O. In all cases the strontium/yttrium atoms center the monocapped trigonal prisms. Note the similarity in the SrX₇ frameworks, and the similarities in the bonding between the layers. In Sr(OD)₂, the hydrogen atoms are displaced out of the gap toward the layer, thus making room for the Sr–O interlayer bonding. In SrBr₂·H₂O, the hydrogen atom positions are unknown, and the oxygen atoms are represented by the small open circles.

gest that it might be rewarding to explore the possibility of hydration/dehydration process in the systems SrBr₂·H₂O and Sr(OH)₂·H₂O. In this connection we remark that "SrBr₂·H₂O" was originally reported to be anhydrous, but with otherwise the same structure (13), although later work reports a different structure for the anhydrous salt (14). A recent report of a metastable form IV of SrI₂ (15) with the same structure as Sr(OH)₂ (see

TABLE 2

Selected Interatomic Distances, Corrected for Riding Motion, Bond Valences, and Bond Valence Sums for both the Uncorrected and Corrected Bond Lengths

Bond	Length	Valence
Sr–O(1)	2.560(2) (2×)	0.303 (2×)
Sr–O(1)	2.640(3)	0.244
Sr–O(1)	2.730(3)	0.191
Sr–O(2)	2.540(2) (2×)	0.320 (2×)
Sr–O(2)	2.573	0.293
Bond valence sum at Sr		1.972
O(1)–D(2)	0.986	0.906
Corrected ^a	1.030	0.806
O(2)–D(1)	0.819	1.424
Corrected ^a	0.860	1.275

^a Using the "riding-motion" approximation (8).

TABLE 3

Atomic Coordinates in SrBr₂·H₂O (left) and SrI₂ (below) Compared With Those for SrO₂H₂ [Sr(OH)₂] (right); The Space Group is *Pnma* for All Crystals

<i>a</i> = 11.39, <i>b</i> = 4.28, <i>c</i> = 9.19 Å				<i>a</i> = 9.827, <i>b</i> = 3.95, <i>c</i> = 6.073 Å			
Sr	0.1906	1/4	0.8845	Sr	0.1587	1/4	0.8968
Br(1)	0.3981	1/4	0.6143	O(1)	0.3918	1/4	0.6523
Br(2)	0.3850	1/4	0.1544	O(2)	0.3735	1/4	0.1390
O	0.175	1/4	0.379				
SrI ₂ Form IV (15)							
<i>a</i> = 12.328, <i>b</i> = 4.920, <i>c</i> = 8.384 Å							
Sr	0.170	1/4	0.870				
I(1)	0.392	1/4	0.623				
I(2)	0.320	1/4	0.117				

Table 3 and Fig. 3) suggests that SrBr₂ might also be polymorphic.

ACKNOWLEDGMENT

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