Distance Limits of OH···Y Hydrogen Bonds (Y = Cl, Br, I) in Solid Hydroxides. Structure Refinement of Laurionite-Type Ba(OD)I, Sr(OD)I and Sr(OH)I by Neutron and Synchrotron X-ray Powder Diffraction

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Abstract

Synchrotron X-ray and neutron powder diffraction experiments on Sr(OH)I, Sr(OD)I and Ba(OD)I have been performed at ambient temperature. The structure data obtained by Rietveld refinement confirm the laurionite-type structure {$Pnma$, $Z = 4$; R_I = 5.9, 7.9 and 7.8%; a = 7.7294 (1), b = 4.24697 (7) and c = 10.7374 (1) Å [Sr(OH)I]; a = 7.7303 (8), b = 4.2465 (4) and c = 10.7399 (10) Å [Sr(OD)I]; a = 8.0291 (9), b = 4.4961 (5) and c = 11.0196 (16) Å [Ba(OH)I]; a = 8.0203 (13), b = 4.4912 (7) and c = 11.0193 (14) Å [Ba(OD)I]} proposed from IR and Raman spectra. In contrast to the respective lead compound, only very weak hydrogen bonds are formed. The strength of the hydrogen bonds of OH⁻ ions in condensed material is discussed with respect to intermolecular H···Y distances, furcation of the bonds and M—O bond lengths (synergetic effect). The longest H···Y distances (Y = Cl, Br, I), for which hydrogen bonds due to OH⁻ have been established, are 2.80, 2.90 and 3.25 Å, respectively.

1. Introduction

The hydroxide iodides M(OH)I, with M = Sr and Ba, were first prepared in 1991 (Beckenkamp, 1991). X-ray powder diffraction and IR and Raman spectroscopic studies (Lutz, 1995; Lutz, Beckenkamp & Peter, 1995) revealed a laurionite (Pb(OH)Cl)-type (Brasseur, 1940) structure for the title compounds. In addition, an unusual change of the strengths of the H···Y hydrogen bonds formed within the isotypic M(OH)Y series [M = Ba, Pb; Y = Cl, Br, I; Sr(OH)I] was observed. Thus, in the case of the lead compounds, relatively strong hydrogen bonds are formed with the lone pair of Pb²⁺ acting as a hydrogen-bond acceptor (Möller, Beckenkamp, Kellersohn & Lutz, 1992), whereas the respective strontium and barium hydroxide halides form weak or even very weak hydrogen bonds, e.g. Ba(OH)Cl, or do not

at all, e.g. Ba(OH)Br (Möller, Beckenkamp, Kellersohn, Lutz & Cockcroft, 1994). Therefore, these and related compounds are particularly suitable for studying the limits of hydrogen bonding in solid hydroxides (Lutz, 1995). For this, *i.e.* for accurate H···Y distances, however, neutron diffraction data are absolutely essential. We therefore performed neutron and synchrotron X-ray diffraction experiments on polycrystalline M(OD)I (M = Sr, Ba) and Sr(OH)I. The respective structure data of Ba(OD)Y (Y = Cl, Br) and Pb(OD)Y (Y = Cl and I) are given in Möller *et al.* (1994) and Möller (1993).

2. Experimental

Polycrystalline samples of Sr(OH)I and M(OD)I (M = Sr, Ba) were prepared by sintering stoichiometric mixtures of anhydrous M(OX)₂ (X = H, D) and MI₂ under argon in carbon glass crucibles at 920–930 K [Sr(OX)I] and 770–780 K [Ba(OD)I], respectively.

Neutron diffraction experiments on M(OD)I were performed at ambient temperature with the high-resolution 3T2 powder diffractometer at the Orphee reactor of the Laboratoire Léon Brillouin (LLB), Saclay, with the samples taken in vanadium containers. The measurements were made with neutron wavelengths λ = 1.2259 [Sr(OD)I] and 1.2272 Å [Ba(OD)I], respectively. After rescaling, refinements of profile, positional and isotropic and anisotropic mean square displacement parameters were performed with the Rietveld program *PROFIL* (Cockcroft, 1993). The starting values of M, O, D and I were taken from the positional parameters of the isotypic Ba(OD)Cl (Möller *et al.*, 1994). The scattering lengths were b(Ba) = 5.07, b(Sr) = 7.02, b(O) = 5.805, b(I) = 5.28 and b(D) = 6.674 fm, respectively (Koester & Rauch, 1983).

Synchrotron X-ray powder diffraction experiments on Sr(OH)I were performed at ambient temperature with the powder diffractometer 9.1 at the SRS, Daresbury, with the sample sealed in a 0.3 mm capillary. The data were collected over the 2θ range 5–70° in steps of 0.01° at 2 s per point with λ = 0.85 Å. The background was determined graphically by 73 data points. Structure refinement was established with the Rietveld program

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Table 1. *Profile and structural parameters of Sr(OH)I, Sr(OD)I and Ba(OD)I*

	Sr(OH)I	Sr(OD)I*	Ba(OD)I*
a (Å)	7.7294 (1)	7.7303 (8)	8.0203 (13)
b (Å)	4.24697 (7)	4.2465 (4)	4.4912 (7)
c (Å)	10.7374 (1)	10.7399 (10)	11.0193 (14)
V (Å^3)	352.47 (1)	352.81 (3)	396.72 (4)
D_{calc} (g cm^{-3})	4.362	4.358	4.708
U (°^{2})	0.009 (4)	0.30 (1)	0.30 (2)
V (°^{2})	0.002 (1)	−0.35 (1)	−0.29 (2)
W (°^{2})	0.0011 (1)	0.144 (4)	0.121 (4)
Observations	1369	802	831
Reflections	209	541	557
Degrees of freedom	1344	753	800
Parameters	16	25	25
Pseudo-Voigt (Lorentz/Gauss)	0.3195 (35)	0.1338 (10)	0.1710 (11)
Asymmetry	37.49 (65)	1.03 (1)	1.53 (2)
R_{wp}	14.3	10.1	10.7
R_I	5.9	7.9	7.8
R_{exp}	5.2	9.6	8.9
λ (Å)	0.85	1.2259	1.2272
2θ (°)	5–50	5–110	5–110
Atom %D	0	63	91
Impurity (wt-%)		SrCO$_3$ (5.6)	Al (1.4)

* Unit-cell dimensions from X-ray Guinier powder diffraction photographs.

PROFIL (Cockcroft, 1993) using scattering factors for neutral atoms f_0 (Cromer & Waber, 1974). The anomalous dispersion values of Sr and I were taken into account by the equation

$$f^{anom} = f_0 + f' + if'', \qquad (1)$$

with f' and f'' equal to −2.074 and 0.629 (Sr) and −0.49 and 2.489 (I), respectively (Creagh & McAuley, 1992). Starting parameters were taken from isotypic Ba(OD)Cl (Möller *et al.*, 1994). For further details see Table 1.*

3. Results

The observed and fitted diffraction patterns of Sr(OH)I, Sr(OD)I and Ba(OD)I are shown in Fig. 1. As shown by structure refinement, the samples of Sr(OD)I and Ba(OD)I were contaminated by 5.6 and 1.4 wt-% SrCO$_3$ and Al, respectively. The deuterium levels were refined to 63 and 91 atom-%, respectively. The final R values based on 1369, 802 and 831 observations containing 209, 541 and 557 reflections and 1369, 753 and 800 degrees of freedom are R_{wp} = 14.3, 10.1 and 10.7%, R_{exp} = 5.2, 9.6 and 8.9% and R_I = 5.9, 7.9 and 7.8%. The final profile parameters are given in Table 1, the structural parameters in Table 2 and selected distances and angles are given in Table 3. The laurionite-type

Table 2. *Fractional parameters and equivalent thermal parameters (Å^2) of Sr(OH)I (synchrotron X-ray), Sr(OD)I and Ba(OD)I (both neutron); all atoms are on position 4(c)*

$$B_{eq} = 4/3 \sum_i \sum_j \beta_{ij} a_i a_j$$

		x	y	z	B_{eq}
Sr(OH)I	Sr	0.1789 (4)	1/4	0.0789 (3)	1.48 (8)
	O	0.365 (2)	1/4	0.473 (1)	1.0 (4)*
	I	0.0226 (2)	3/4	0.3193 (1)	1.49 (6)
Sr(OD)I	Sr	0.1781 (5)	1/4	0.0769 (3)	1.64 (6)
	O	0.3664 (6)	1/4	0.4677 (4)	1.73 (5)
	D	0.2834 (7)	1/4	0.4038 (5)	3.3 (1)
	I	0.0220 (7)	3/4	0.3196 (3)	1.64 (9)
Ba(OD)I	Ba	0.1893 (6)	1/4	0.0808 (5)	2.03 (9)
	O	0.3697 (5)	1/4	0.4658 (4)	1.70 (7)
	D	0.2906 (7)	1/4	0.4008 (5)	4.8 (2)
	I	0.0282 (7)	3/4	0.3185 (4)	1.99 (9)

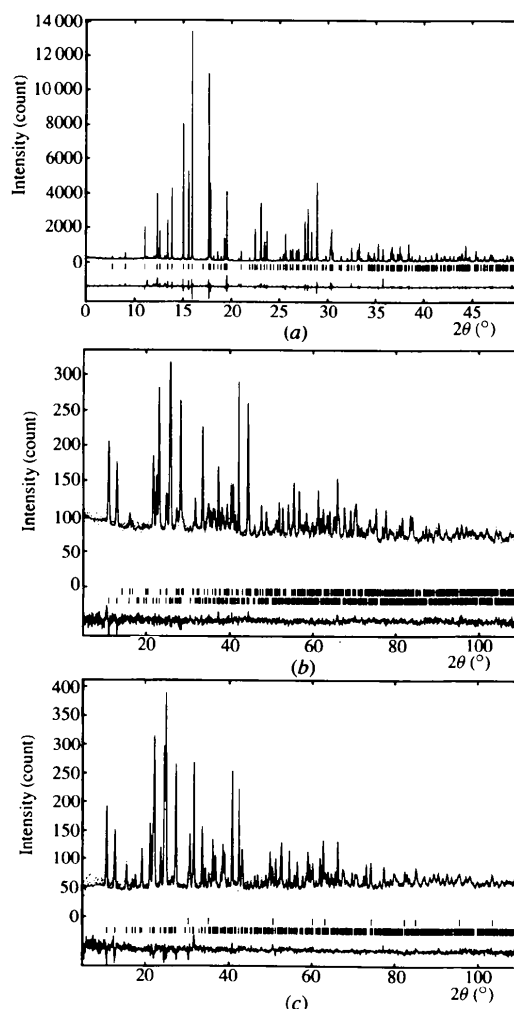* Isotropic temperature factor (B_{iso})

Fig. 1. (*a*) Synchrotron X-ray diffraction pattern of Sr(OH)I, (*b*) neutron diffraction pattern of Sr(OD)I and (*c*) Ba(OD)I at 295 K [......, observed; ____, fitted (*PROFIL*), difference profile; I, reflections; first row, impurity as mentioned in the text].
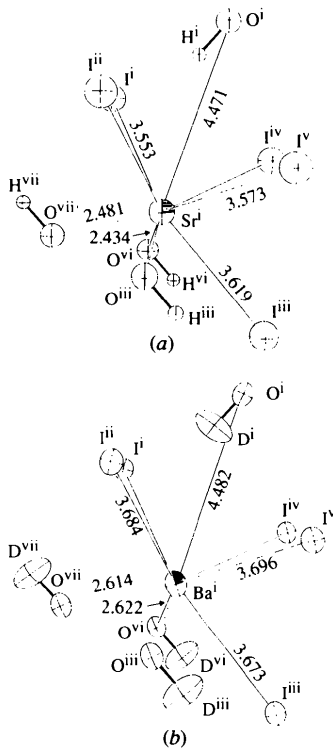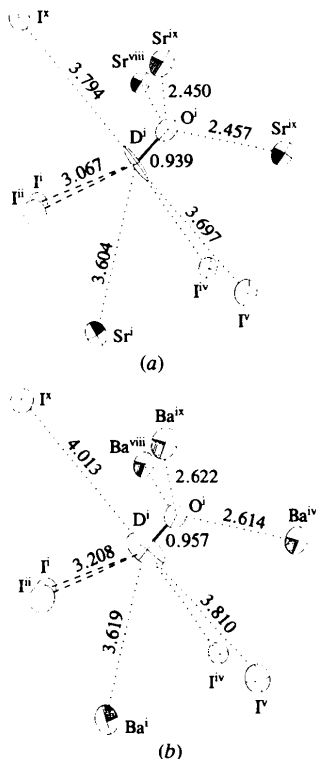
Fig. 2. Coordination geometries of the metal ions in (a) Sr(OH)I (synchrotron X-ray data, hydrogen position from neutron data) and (b) Ba(OD)I (neutron data); probability 50%; distances in Å.

Fig. 3. Hydrogen bonds (- - -) in (a) Sr(OD)I and (b) Ba(OD)I; · · ·, other intermolecular distances (Å, neutron data).

Table 3. *Selected interatomic distances (Å) and angles (°)*

	Sr(OH)I*	Sr(OD)I†	Ba(OD)I†
$M\{O(H,D)\}_4I_5$ polyhedron			
$M^i - I^{i,ii}$	3.553 (3)	3.572 (4)	3.684 (5)
$M^i - I^{iii}$	3.619 (3)	3.607 (6)	3.673 (7)
$M^i - I^{iv,v}$	3.573 (3)	3.579 (5)	3.696 (6)
$M^i - O^i$	4.471 (12)	4.442 (5)	4.482 (7)
$M^i - O^{iii,vi}$	2.434 (6)	2.450 (3)	2.622 (4)
$M^i - O^{vii}$	2.481 (16)	2.457 (6)	2.614 (6)
$M^i - D^i$		3.604 (6)	3.619 (8)
$I^i - M^i - I^{ii}$	73.38 (6)	72.94 (8)	75.11 (11)
$I^{i,ii} - M^i - I^{iv,v}$	71.06 (10)	70.83 (11)	70.98 (12)
$I^{iii} - M^i - I^{iv,v}$	76.20 (8)	76.15 (11)	77.44 (13)
$I^{iv} - M^i - I^v$	72.94 (7)	72.77 (10)	74.82 (12)
$I^{i,ii} - M^i - O^{iii,vi}$	76.73 (25)	77.69 (11)	76.01 (12)
$I^{i,ii} - M^i - O^{vii}$	80.29 (22)	79.10 (14)	78.22 (16)
$I^{iii} - M^i - O^{iii,vi}$	74.27 (23)	73.95 (13)	74.39 (15)
$I^{iii} - M^i - O^{vii}$	116.68 (24)	118.75 (17)	116.76 (22)
$M^i - O^i - D^i$		23.95 (40)	22.70 (40)
O(H,D) coordination			
$O^i - D^i$		0.939 (7)	0.957 (7)
$D^i - I^{i,ii}$		3.067 (5)	3.208 (6)
$D^i - I^{iv,v}$		3.697 (6)	3.810 (6)
$D^i - I^{viii}$		3.794 (7)	4.013 (7)
$O^i - I^{i,ii}$	3.778 (12)	3.758 (6)	3.896 (6)
$O^i - I^{iv,v}$	3.980 (13)	3.934 (5)	4.059 (5)
$O^i - I^{viii}$	3.742 (14)	3.773 (7)	3.979 (7)
$O^i - D^i - I^{i,ii}$		131.70 (20)	130.28 (21)
$O^i - D^i - I^{iv,v}$		97.66 (37)	98.23 (36)
$O^i - D^i - I^{vii}$		81.55 (43)	81.11 (42)
$M^{iv} - O^i - M^{ix,x}$	104.1 (4)	103.36 (12)	105.78 (15)
$M^{vii} - O^i - M^{ix}$	121.5 (5)	120.15 (20)	117.87 (22)

Symmetry code(s): (i) x, y, z; (ii) $x, y - 1, z$; (iii) $\frac{1}{2} - x, -\frac{1}{2} + y, -\frac{1}{2} + z$; (iv) $\frac{1}{2} + x, y, \frac{1}{2} - z$; (v) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$; (vi) $\frac{1}{2} - x, \frac{1}{2} + y, -\frac{1}{2} + z$; (vii) $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$; (viii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$; (ix) $\frac{1}{2} - x, -y, \frac{1}{2} + z$; (x) $-x, 1 - y, 1 - z$. * Synchrotron X-ray data. † Neutron data.

structures of the title compounds revealed from IR and Raman spectroscopic studies (Möller *et al.*, 1992; Lutz *et al.*, 1995) have been confirmed. The coordination geometries of the Sr^{2+}, Ba^{2+} and the OD⁻ ions are shown in Figs. 2 and 3.

4. Discussion

4.1. *Laurionite-type structures of M(OX)I (M = Sr, Ba; X = H, D)*

The structures of Sr(OH)I and Ba(OH)I are similar to that of Ba(OH)Br, but differ from those of the isotypic Ba(OH)Cl (Möller *et al.*, 1994) and Pb(OH)Y [Y = Cl, Br, I (Möller *et al.*, 1992; Möller, 1993)], in particular with respect to orientation of the OH⁻ ions in the structure and strength and geometry of the hydrogen bonds. The title compounds form extremely weak (if at all), bifurcated (three-centre) or even fourfurcated (five-centre) hydrogen bonds to adjacent halide ions, whereas the hydrogen bonds present in the lead compounds are relatively strong due to the large synergetic effect of Pb^{2+} ions (Lutz *et al.*, 1995).

The coordination of the metal ions is a tricapped trigonal prism of five halide and four hydroxide ions with one OH⁻ coordinated *via* the H atom (see Fig. 2). This coordination is obviously favourable for Ba^{2+} and Pb^{2+} ions, but not for Sr^{2+} and still smaller metal ions. Thus, Sr(OH)Cl crystallizes in the Cd(OH)Cl type [as well as Ca(OH)Cl], whereas Sr(OH)Br possesses its own cubic structure type. Both structures show monocapped $Sr(OH)_3Y_4$ octahedra (Peter & Lutz, 1996).

The interionic D···I distances of Ba(OD)I are significantly longer (> 3.20 Å) than those of Sr(OD)I (some bond lengths < 3.10 Å, see Table 3 and Fig. 3). This would suggest that the hydrogen bonds in Ba(OD)I are weaker than those of the strontium compound. However, the wavenumbers of the uncoupled OD stretching modes recorded in isotopically dilute samples are 2651 [Ba(OD)I] and 2653 cm⁻¹ [Sr(OD)I], respectively. Thus, the vibrational spectra reveal that the hydrogen bonds in Ba(OD)I are at least equally strong as or even stronger than in the strontium compound (Lutz *et al.*, 1995).

The structure data obtained for Sr(OH)I and Sr(OD)I as well as the unit-cell dimensions of *M*(OH)I and *M*(OD)I differ slightly (see Tables 2 and 3). Hence, structural isotope effects may be present, but to a much smaller extent than observed for Ba(O*X*)Cl (Möller *et al.*, 1994).

4.2. Distance-limits of H···Y (Y = Cl, Br, I) hydrogen bonds

After Mikenda (1986) hydrogen bonds to halide ions as acceptor groups range within intermolecular H···*Y* distances of 1.85–2.40 (Cl), 2.30–2.50 (Br) and 2.55–2.90 Å (I). In laurionite-type and other structure-type *M*(OH)*Y*, however, much longer and weaker hydrogen bonds are formed. Therefore, the question arises what the distance limits of such hydrogen bonds are and if a borderline distance can be derived as it has been established for H···O hydrogen bonds, *viz.* 2.30–2.40 Å (Lutz *et al.*, 1994; Alig, Lösel & Trömel, 1994).

As proposed in 1992 (Beckenkamp & Lutz, 1992; Lutz *et al.*, 1994), the strength of hydrogen bonds in condensed material is related to the low-energy shift of the OH stretching modes relative to those calculated for OH⁻ ions, which do not donate hydrogen bonds. The latter are governed by the mean *M*—O distances of the first M_xOH coordination sphere (Beckenkamp & Lutz, 1992). Using the ν(OH) *versus* $\overline{r_{M-O}}$ correlation curve established in this paper, OH stretching modes of 3608 and 3622 cm⁻¹ would correspond to the respective mean *M*—O distances of Ba(OH)I and Sr(OH)I; hence, the low-energy shifts of the observed bands (3590 and 3592 cm⁻¹) are 18 and 30 cm⁻¹, respectively. Therefore, very weak, but nevertheless, real hydrogen bonds cannot be excluded in both compounds (Lutz *et al.*, 1995), despite the large D···I distances. The slightly smaller D···I

distances of Sr(OD)I compared with Ba(OD)I are caused by the stronger synergetic effect (Lutz, 1988) of the smaller Sr^{2+} ions.

The large distances (see above) are compatible with the formation of hydrogen bonds, because the bonds formed by the title compounds are at least bifurcated (three-centre; see Fig. 3), and bifurcated and higher furcated hydrogen bonds are stronger than equally long single (two-centre) hydrogen bonds (Möller, Kellersohn, Schmidt, Lutz & Cockcroft, 1993). From these results we suggest that intermolecular H···I distances of 3.25 Å are the upper distance limit of hydrogen bonds producing low-energy shifts of the O*X* stretching modes. Furthermore, we propose the corresponding H···Cl and H···Br hydrogen-bond distance limits being 2.80 and 2.90 Å, respectively. The respective H···Y van der Waals distances are 3.00, 3.15 and 3.35 Å (Weast, 1986).

5. Conclusions

Laurionite-type hydroxide halides are a series of model compounds which make it possible to elucidate the nature, structure and the limits of weak H···*Y* (*Y* = Cl, Br, I) hydrogen bonds. Hence, (i) the stronger synergetic effect of Sr^{2+} ions compared with that of Ba^{2+}, (ii) the greater strength of bifurcated hydrogen bonds compared with single ones and (iii) the validity of the ν(OH) *versus* $\overline{r_{M-O}}$ correlation curve for OH⁻ ions not involved in hydrogen bonds has been confirmed. The longest H···*Y* distances, for which hydrogen bonds have been established, are 2.80, 2.90 and 3.25 Å, respectively.

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