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Hydrothermal Preparation and Crystal Structure of $NaHo_4(GeO_4)_2O_2OH$

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The compound $NaHo_4(GeO_4)_2O_2OH$ was prepared using hydrothermal techniques. The crystal structure was investigated using Patterson and Fourier functions and was refined to a conventional R value of 8.5 %. The space group is *Pnma* with $a = 6.75$ Å, $b = 21.67$ Å, and $c = 6.91$ Å. The holmium atoms are seven coordinated with oxygen atoms.

A hydrothermal investigation of the system $Ho_2O_3 - H_2O - Na_2O$ yielded the monoclinic form of holmium oxide hydroxide and single crystals of a phase of unknown composition in one experiment, where the system was contaminated with a small quantity of germanium dioxide. A three-dimensional X-ray analysis proved that this new phase had the formula $NaHo_4(GeO_4)_2O_2OH$.

EXPERIMENTAL

Chemistry. Holmium trihydroxide was precipitated with a 2 M NH_3 solution from a dilute solution of holmium nitrate, prepared by dissolving the oxide in nitric acid. The precipitated trihydroxide was washed with water, and was treated with a 1.5 M NaOH solution at 490°C, 1200 atm for 60 h in a pressure bomb lined with pure silver. The product was washed with water and dried in air at room temperature. The silver ampoule had previously been used in hydrothermal preparation of germanates.

X-Ray technigue. A flat crystal with dimensions 0.0175 cm × 0.0063 cm × 0.0023 cm was investigated using Weissenberg and precession methods. Photographs were taken of (0*kl*), (1*kl*), (2*kl*), (*hk*0), and (*h*0*l*) using Ni-filtered Cu$K\alpha$ radiation. A total of 934 independent *hkl* reflections with $I > 2\sigma(I)$ were measured with a diffractometer of the Arndt Phillips design using Mo$K\alpha$ radiation monochromated by reflection from a graphite crystal and using a scintillation counter in conjunction with a pulse height analyser. Lorentz polarization corrections were applied and absorption correction was made using Well's method.[1]

STRUCTURE DETERMINATION

The symmetry of the Weissenberg and precession photographs is in agreement with the space group *Pnma* (No. 62). A three-dimensional Patterson function gave the positions (0.22, 0.01, 0.12), and (0.40, 0.15, 0.37) for two hol-

mium atoms. A three-dimensional Fourier map phased on this assumption gave the position (0.42, 0.14, 0.87) of the germanium atom. A new Fourier map based on structure factor signs calculated with all the heavy atoms gave the positions of all the oxygen atoms and the sodium atom. The refinement proceeded by the methods of least squares (G 403),[2] using isotropic temperature factors, giving an R-value of 8.5 %. A final difference Fourier map showed no extra atoms.

Table 1. Atomic coordinates and temperature factors with standard deviations. Diffractometer data, 934 reflections, $R = 8.5$ %.

Atom	x	y	z	B (Å^2)
O_1	0.221 (3)	0.1163 (9)	0.075 (3)	0.3 (3)
O_2	0.390 (3)	0.0438 (9)	0.384 (3)	0.3 (3)
O_3	0.48 (1)	0.25 (0)	0.342 (9)	6.3 (1.5)
O_4	0.087 (3)	0.1589 (9)	0.427 (3)	0.5 (3)
O_5	0.390 (4)	0.173 (1)	0.709 (3)	1.1 (4)
O_6	0.454 (3)	0.0466 (9)	0.859 (3)	0.6 (3)
Na	0.150 (2)	0.25 (0)	0.694 (2)	0.0 (2)
Ge	0.4214 (5)	0.1258 (2)	0.9103 (4)	0.60 (5)
Ho_1	0.2201 (2)	0.01227 (6)	0.1258 (2)	0.43 (2)
Ho_2	0.4080 (2)	0.15002 (7)	0.3774 (2)	0.55 (2)

Table 2. Interatomic distances in Å and bond angles in degress. Standard deviations in parentheses.

$Ge-O_1$	1.780	(20)	O_1-Ge-O_5	119.3 (9)
$Ge-O_5$	1.741	(23)	O_1-Ge-O_4'	96.9 (8)
$Ge-O_4'$	1.744	(21)	O_1-Ge-O_6	96.3 (8)
$Ge-O_6$	1.766	(21)	O_5-Ge-O_4'	110.6 (9)
			O_5-Ge-O_6	115.2 (9)
Ho_1-O_2'	2.333	(20)	$O_4'-Ge-O_6$	116.8 (8)
Ho_1-O_2''	2.194	(19)		
Ho_1-O_6''	2.366	(20)	$O_1-Ho_1-O_2'$	73.1 (8)
Ho_1-O_1	2.281	(21)	$O_1-Ho_1-O_6''$	119.8 (8)
Ho_1-O_2	2.229	(19)	$O_2'-Ho_1-O_6''$	167.0 (8)
Ho_1-O_6	2.537	(20)	$O_6'-Ho_1-O_2''$	93.0 (8)
Ho_1-O_6''	2.547	(22)	$O_2-Ho_1-O_6$	100.0 (8)
Ho_2-O_1	2.545	(19)		
			$O_1-Ho_2-O_4'$	64.0 (8)
Ho_2-O_4	2.199	(22)	$O_1-Ho_2-O_5$	146.8 (8)
Ho_2-O_2	2.305	(20)	$O_4'-Ho_2-O_5$	148.3 (8)
Ho_2-O_4'	2.432	(20)	$O_2-Ho_2-O_4$	91.8 (8)
Ho_2-O_3	2.236	(18)	$O_1'-Ho_2-O_2$	97.0 (9)
Ho_2-O_1'	2.262	(20)		
Ho_2-O_5	2.347	(22)		
$Na'-O_3$	3.402	(50)		
$Na'-O_5$	2.510	(27)		
$Na'-O_4'$	2.738	(23)		
$Na'-O_5'$	2.330	(27)		
$Na'-O_3'$	2.459	(50)		

Table 3. Observed and calculated structure factors.

h	k	l	Fo	Fc
0	4	0	121	-166
0	6	0	657	821
0	8	0	604	701
0	10	0	278	-264
0	12	0	188	178
0	14	0	302	350
0	20	0	185	198
0	22	0	105	-115
0	24	0	68	-101
0	28	0	121	-130
0	3	1	155	-139
0	5	1	152	134
0	7	1	298	-300
0	9	1	332	-363
0	13	1	154	-172
0	15	1	460	-538
0	17	1	74	-72
0	21	1	330	-390
0	23	1	241	-261
0	25	1	65	70
0	27	1	136	-180
0	29	1	208	-241
0	0	2	73	79
0	2	2	56	40
0	4	2	185	-175
0	6	2	35	24
0	8	2	88	97
0	12	2	125	-113
0	14	2	58	43
0	20	2	57	-46
0	28	2	48	-50
0	1	3	287	-246
0	3	3	64	-55
0	5	3	104	100
0	7	3	352	-358
0	9	3	328	-300
0	11	3	154	150
0	13	3	267	-265
0	15	3	454	-478
0	21	3	357	-418
0	23	3	207	-257
0	25	3	55	74
0	27	3	108	-135
0	0	4	932	-926
0	2	4	324	-312
0	4	4	38	33
0	6	4	612	-593
0	8	4	467	-468
0	10	4	141	136
0	12	4	150	-144
0	14	4	365	-360
0	16	4	57	62
0	20	4	186	-209
0	22	4	60	75
0	24	4	132	156
0	1	5	210	203
0	3	5	129	125
0	5	5	148	-142
0	7	5	171	149
0	9	5	324	315
0	13	5	106	93
0	15	5	346	332
0	17	5	168	169
0	19	5	68	66
0	21	5	231	238
0	23	5	175	185
0	0	6	165	-166
0	4	6	193	198
0	6	6	45	-41
0	8	6	123	-123
0	12	6	110	111
0	16	6	61	-61
0	20	6	87	72
0	1	7	147	159
0	3	7	44	48
0	5	7	53	-52
0	7	7	224	203
0	9	7	229	223
0	11	7	91	-78
0	13	7	151	136
0	15	7	334	322
0	17	7	63	41
0	0	8	453	419
0	2	8	203	200
0	4	8	84	77
0	6	8	383	377
0	8	8	227	199
0	10	8	66	-53
0	12	8	182	170
0	14	8	257	256
0	16	8	102	-111
0	1	9	175	-161
0	3	9	102	-93
0	5	9	110	98
1	3	1	119	-118
1	4	1	27	17
1	5	1	221	-220
1	6	1	234	238
1	7	1	36	13
1	9	1	95	-95
1	10	1	163	-168
1	11	1	396	-425
1	12	1	193	205
1	13	1	165	-187
1	14	1	141	168
1	15	1	40	-28
1	16	1	198	-233
1	17	1	260	-296
1	18	1	44	-45
1	19	1	301	-345
1	20	1	211	239
1	21	1	70	-66
1	22	1	48	-46
1	23	1	106	-113
1	24	1	180	-196
1	25	1	224	-253
1	26	1	82	99
1	27	1	120	-129
1	28	1	96	90
1	0	2	124	-114
1	1	2	469	-452
1	2	2	478	-469
1	3	2	289	-284
1	4	2	668	-666
1	5	2	301	306
1	6	2	160	-159
1	7	2	55	-42
1	8	2	246	-234
1	9	2	464	-468
1	10	2	504	-519
1	11	2	109	92
1	12	2	235	-239
1	13	2	139	153
1	15	2	175	-187
1	16	2	199	-214
1	17	2	54	-50
1	18	2	86	-101
1	19	2	95	109
1	20	2	85	105
1	21	2	127	-148
1	26	2	158	188
1	27	2	109	-137
1	28	2	100	98
1	29	2	109	-134
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1	2	3	45	42
1	3	3	47	45
1	4	3	140	129
1	5	3	240	228
1	6	3	274	-254
1	7	3	102	99
1	8	3	80	-80
1	9	3	51	45
1	10	3	159	153
1	11	3	318	307
1	12	3	130	-119
1	13	3	199	199
1	14	3	156	-162
1	15	3	110	108
1	16	3	145	145
1	17	3	219	223
1	19	3	263	277
1	20	3	125	-136
1	21	3	93	96
1	23	3	136	146
1	24	3	91	121
1	25	3	177	213
1	26	3	63	-84
1	27	3	115	115
1	0	4	102	106
1	1	4	72	-72
1	2	4	38	-36
1	3	4	94	-101
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1	8	4	47	50
1	9	4	65	-55
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1	11	4	83	-84
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1	5	5	171	163
1	6	5	166	-153
1	9	5	90	83
1	10	5	164	158
1	11	5	287	278
1	12	5	162	-159
1	13	5	181	177
1	14	5	142	-136
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1	19	5	281	274
1	20	5	228	-232
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1	23	5	63	76
1	24	5	159	162
1	25	5	213	233
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1	2	6	350	336
1	3	6	132	134
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1	6	6	132	137
1	7	6	120	131
1	8	6	174	161
1	9	6	254	233
1	10	6	365	352
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1	12	6	133	122
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1	16	6	157	153
1	18	6	84	76
1	19	6	89	-90
1	20	6	93	-104
1	21	6	143	144
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1	10	7	119	-110
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1	19	7	194	-167
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1	7	8	55	-63
1	8	8	51	-44
1	9	8	70	72
1	13	8	62	-61
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1	6	9	131	135
1	10	9	131	-117
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2	5	0	471	-532
2	6	0	155	-190
2	7	0	55	42
2	8	0	214	-221
2	9	0	250	289
2	10	0	431	-484
2	11	0	243	-256
2	12	0	207	-239
2	13	0	308	-332
2	15	0	88	75
2	16	0	144	-148
2	17	0	140	-146
2	18	0	92	-86
2	19	0	210	-241
2	20	0	58	56
2	24	0	57	47
2	25	0	181	-205
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2	8	1	34	-41
2	9	1	109	106
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2	21	3	59	62
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2	24	3	149	-171
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2	8	4	181	174
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2	2	5	173	155
2	4	5	292	277
2	5	5	191	-187
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2	7	5	139	-130
2	9	5	52	-51
2	10	5	254	235
2	11	5	196	-171
2	13	5	188	-182
2	14	5	81	-83
2	15	5	121	-112
2	16	5	123	118
2	17	5	154	-150
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2	19	5	178	-178
2	20	5	110	-104
2	21	5	122	-113
2	23	5	130	-137
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2	5	6	70	66
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2	8	6	66	-60
2	9	6	92	-87
2	11	6	57	-45
2	13	6	70	62
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2	17	6	83	-67
2	0	7	66	-52
2	2	7	100	94
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2	6	7	98	-93
2	8	7	80	79
2	9	7	73	-70
2	10	7	211	203
2	11	7	203	-190
2	12	7	61	-48
2	13	7	127	-117
2	14	7	101	-90
2	16	7	198	193
2	17	7	184	-173
2	19	7	211	-188
2	20	7	194	-166
2	0	8	117	-116
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2	2	8	245	-226
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2	4	8	277	-257
2	5	8	221	-194
2	6	8	139	-130
2	8	8	148	-141
2	9	8	115	117
2	10	8	239	-224
2	11	8	234	-225
2	12	8	111	-98
2	15	8	115	-103
2	15	8	98	91
2	16	8	130	-112
2	0	9	142	116
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2	2	9	102	-84
2	4	9	237	-218
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3	4	1	65	-71
3	5	1	134	-117
3	6	1	177	-176
3	7	1	299	304
3	8	1	125	-122
3	9	1	266	267
3	10	1	47	-53
3	11	1	134	-137
3	13	1	180	201
3	14	1	76	-74
3	15	1	390	441
3	18	1	42	-29
3	19	1	43	-41
3	21	1	324	367
3	23	1	197	210
3	24	1	46	31
3	25	1	68	-86
3	27	1	99	124
3	0	2	1005	972
3	1	2	74	65
3	2	2	268	256
3	3	2	59	57
3	4	2	177	-166
3	5	2	43	29
3	6	2	618	579
3	7	2	98	96
3	8	2	501	491
3	9	2	183	169
3	10	2	183	-176
3	11	2	99	90
3	12	2	89	85
3	13	2	142	142
3	14	2	344	346
3	15	2	190	186
3	17	2	138	134
3	19	2	83	94
3	20	2	148	177
3	21	2	155	178
3	22	2	65	-84
3	23	2	118	120
3	24	2	106	-123
3	26	2	70	105
3	0	3	202	184
3	1	3	235	-214
3	2	3	185	171
3	3	3	95	-89
3	4	3	91	77

Table 3. Continued.

3	5	3	152	137
3	6	3	196	183
3	7	3	214	-191
3	8	3	74	70
3	9	3	307	-289
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3	11	3	66	45
3	12	3	58	48
3	13	3	140	-125
3	14	3	92	82
3	15	3	345	-341
3	17	3	104	-100
3	21	3	244	-268
3	23	3	157	-176
3	24	3	50	-41
3	0	4	199	196
3	3	4	35	26
3	4	4	179	-170
3	6	4	53	39
3	7	4	39	27
3	8	4	115	117
3	9	4	37	-20
3	10	4	43	-39
3	12	4	76	-74
3	16	4	65	69
3	20	4	70	-63
3	0	5	192	191
3	1	5	124	-106
3	2	5	109	94
3	3	5	60	-50
3	4	5	88	85
3	5	5	73	65
3	6	5	110	93
3	7	5	254	-232
3	8	5	128	129
3	9	5	221	-199
3	11	5	110	99
3	12	5	55	54
3	13	5	141	-129
3	14	5	71	48
3	15	5	396	-373
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3	19	5	59	56
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3	0	6	601	-550
3	2	6	172	-157
3	3	6	58	-56
3	6	6	446	-403
3	7	6	105	-109
3	8	6	277	-256
3	9	6	122	-102
3	10	6	119	112
3	11	6	86	-74
3	12	6	182	-162
3	13	6	112	-92
3	14	6	273	-246
3	15	6	169	-160
3	16	6	83	84
3	17	6	110	-87
3	19	6	94	-94
3	20	6	178	-182
3	21	6	143	-114
3	0	7	126	-121
3	1	7	159	145
3	2	7	109	-90
3	3	7	114	114
3	4	7	98	-99
3	5	7	124	-117
3	6	7	108	-90
3	7	7	80	65
3	8	7	71	-73
3	9	7	259	238
3	11	7	50	47
3	12	7	57	-64
3	14	7	75	-50
3	15	7	241	217
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3	4	8	127	118
3	8	8	103	-90
3	0	9	116	-102
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5	23	2	118	-122
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5	4	3	328	-308
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5	10	5	276	-270
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5	9	6	76	-70
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5	11	6	311	288
5	12	6	92	94
5	13	6	228	207
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5	2	7	171	158
5	4	7	302	277
5	5	7	125	-97
5	7	7	78	-88
5	10	7	200	211
5	11	7	89	-63
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5	1	8	66	-45
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6	6	0	318	-361
6	7	0	156	-180
6	8	0	232	-265
6	9	0	167	-198
6	10	0	163	175
6	11	0	115	-122
6	13	0	147	-183
6	14	0	217	-235
6	15	0	247	-276
6	16	0	68	71
6	17	0	135	-153
6	19	0	128	-156
6	20	0	86	-108
6	21	0	209	-232
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6	6	1	167	-182
6	7	1	118	126
6	8	1	173	-182
6	9	1	158	169
6	11	1	127	-123
6	12	1	77	-78
6	13	1	59	61
6	14	1	95	-101
6	15	1	209	243
6	19	1	82	-87
6	20	1	65	-65
6	21	1	191	212
6	0	2	84	-79
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6	7	2	38	18
6	8	2	74	-68
6	16	2	58	-35
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6	1	3	102	93
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6	3	3	39	17
6	4	3	75	-76
6	5	3	112	-95
6	6	3	206	-200
6	7	3	201	187
6	8	3	163	-158
6	9	3	121	114
6	10	3	51	-50
6	11	3	154	-146
6	12	3	62	-64
6	13	3	96	81
6	14	3	99	-90
6	15	3	274	270
6	16	3	56	-23
6	17	3	72	-68
6	19	3	80	-87
6	0	4	446	421
6	1	4	76	72
6	2	4	48	43
6	3	4	71	71
6	4	4	167	-144
6	6	4	304	275
6	7	4	137	135
6	8	4	219	212
6	9	4	215	195
6	10	4	165	-156
6	11	4	91	100
6	12	4	59	58
6	13	4	149	154
6	14	4	218	201
6	15	4	257	247
6	16	4	66	-76
6	17	4	169	153
6	0	5	218	211
6	1	5	148	-132
6	2	5	158	150
6	3	5	71	-75
6	4	5	125	128
6	5	5	131	119
6	6	5	180	176
6	7	5	70	-59
6	8	5	119	109
6	9	5	187	-167
6	10	5	58	36
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6	12	5	109	96
6	14	5	97	89
6	15	5	167	-154
6	0	6	129	121
6	4	6	103	-104
6	8	6	111	87
6	0	7	209	189
6	1	7	99	-77
6	2	7	113	119
6	6	7	158	149
7	3	1	29	-29
7	4	1	136	-157
7	5	1	126	126
7	6	1	208	-218
7	7	1	57	-70
7	8	1	94	-109
7	9	1	73	-70
7	10	1	45	-34
7	11	1	150	160
7	12	1	170	-188
7	13	1	58	59
7	14	1	105	-132
7	15	1	91	-89
7	16	1	74	71
7	17	1	93	110
7	0	2	166	-159
7	1	2	198	194
7	2	2	127	120
7	3	2	183	184
7	4	2	243	235
7	5	2	141	-123
7	6	2	101	-97
7	7	2	115	104
7	8	2	45	-35
7	9	2	315	310
7	10	2	239	230
7	11	2	131	135
7	13	2	69	70
7	14	2	113	-108
7	15	2	242	255
7	16	2	114	131
7	0	3	267	257
7	1	3	112	101
7	2	3	115	118
7	3	3	62	44
7	4	3	109	101
7	5	3	136	-125
7	6	3	229	213
7	7	3	54	45
7	8	3	161	161
7	9	3	77	67
7	11	3	129	-120
7	12	3	166	144
7	13	3	80	-70
7	14	3	131	130
7	15	3	82	55
7	0	4	59	-51
7	1	4	58	66
7	3	4	55	42
7	5	4	58	43
7	7	4	76	-76
7	9	4	68	60
7	0	5	155	153
7	1	5	89	81
7	2	5	130	124
7	4	5	130	114
7	5	5	107	-95
7	6	5	216	202
7	9	5	85	70
7	0	6	133	110
7	1	6	148	-130
8	4	0	55	96
8	5	0	261	320
8	11	0	260	294
8	3	1	33	-36
8	4	1	234	233
8	8	1	112	133
8	10	1	233	244
8	0	3	57	59
8	1	3	51	-38
8	2	3	197	188
8	4	3	190	173
8	8	3	138	142
8	1	4	185	155

CRYSTAL DATA

The formula of the compound is $NaHo_4(GeO_4)_2O_2OH$, and the unit cell contains four formula units. The crystal system is orthorhombic, and the space group is *Pnma* (No. 62). The axes are $a = 6.75$ Å, $b = 21.67$ Å, $c = 6.91$ Å. The calculated density is 6.60 g/cm^3 and the absorption coefficient for Mo-radiation is 274 cm^{-1}. The structure factors for the oxygen and for the sodium atoms were calculated using atomic scattering factors from Vol. III of *International Tables of X-Ray Crystallography*. The structure factors for the holmium atoms were calculated from the atomic scattering factors reported by Cromer and Mann.[3] The atomic scattering factors were approximated by Bassi [4] polynomials. Atomic coordinates and temperature factors are listed in Table 1, and interatomic distances and bond angles in Table 2. Observed and calculated structure factors are listed in Table 3. Fig. 1 is a projection of the HoO_7 coordination polyhedra on the plane (001), and Fig. 2 shows the coordination of the germanium and the sodium atoms with the oxygen atoms in projection on the same plane.

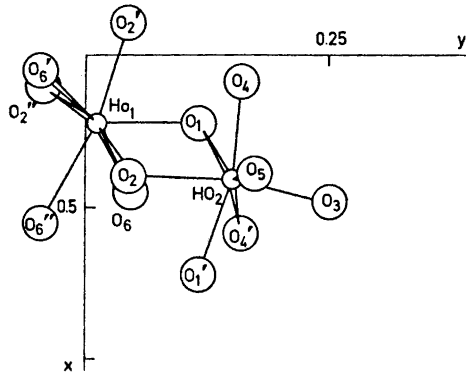

Fig. 1. Projection of the HoO_7 coordination polyhedra on (001).

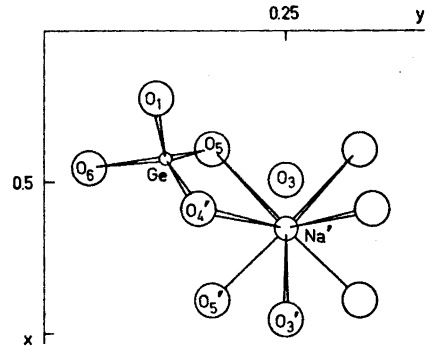

Fig. 2. Projection of the GeO_4 coordination polyhedron and the sodium-oxygen coordination polyhedron on (001).

DISCUSSION

The crystal structure of $NaHo_4(GeO_4)_2O_2OH$ comprises HoO_7 polyhedra and GeO_4 tetrahedra. The GeO_4 tetrahedra are fairly regular and the distances from Ge to O_1, O_6, O_4', and O_5 have a mean of 1.758 Å, $\sigma = 0.011$ Å. The distances from Ge to O_1 and O_6 have a mean value of 1.773 Å, $\sigma = 0.015$ Å, and the distances from Ge to O_4' and O_5 have a mean value of 1.743, $\sigma = 0.016$ Å. These distances are comparable with the Ge – O distances found in the quartz modification of GeO_2,[5] and in $Na_4Ge_9O_{20}$,[6] $Na_8Sn_4Ge_{10}O_{30}(OH)_4$,[7] and $Na_4Sn_2Ge_4O_{12}(OH)_4$.[8] The oxygen atoms of the GeO_4 tetrahedra are coordinated to the following atoms: O_1 to Ge, Ho_1, Ho_2, and Ho_2'; O_6 to Ge, Ho_1, Ho_1', and Ho_1''; O_4' to Ge, Ho_2, Ho_2', and Na'; and O_5 to Ge, Ho_2, Na, and Na'. The GeO_4 tetrahedron is thus only linked to the holmium and the sodium coordination polyhedra.

The two holmium atoms are each coordinated with seven oxygen atoms (see Fig. 1). Ho_1 is coordinated with O_6, O_6', and O_6'', which are also coordinated with the germanium atoms, and with O_2, O_2', and O_2''. The oxygen atom O_2 is coordinated tetrahedrally with four holmium atoms, Ho_1, Ho_1', Ho_1'', and Ho_2. The holmium atom Ho_2 is coordinated with O_1, O_1', O_4, O_4', and O_5 which all are coordinated with germanium atoms, with O_2 which is coordinated with holmium atoms only, and with O_3 which is coordinated with one sodium atom. O_3 is assumed to be the oxygen atom in the OH^- ion. The HoO_7 coordination polyhedra are of the same type as the polyhedra found in the monoclinic modification of holmium oxide hydroxide.[9] The polyhedron around Ho_2 is fairly regular. Six oxygen atoms form a trigonal prism, and the seventh atom, O_5, lies along a normal to a prism face (Fig. 1). The polyhedron around Ho_1 is distorted in comparison with the polyhedron of Ho_2 and the polyhedra found in monoclinic holmium oxide hydroxide. Six oxygen atoms form a trigonal prism (Fig. 1) with the seventh atom, O_6'', displaced so that the angle $O_6''-Ho_1-O_2'$ of 167.0° is much greater than the angle $O_1-Ho_2-O_5$ of 146.8°. The coordination polyhedron around Ho_1 could be described as a distorted cube with one corner omitted.

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REFERENCES

1. Wells, M. J. *Acta Cryst.* **13** (1960) 722.
2. Hazell, R. G. Program G 403. Department of Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark.
3. Cromer, D. T. and Mann, J. B. *Acta Cryst.* **A 24** (1968) 321.
4. Bassi, M. G. *Acta Cryst.* **15** (1962) 617.
5. Smith, G. S. and Isaacs, P. B. *Acta Cryst.* **17** (1964) 842.
6. Ingri, N. and Lundgren, G. *Acta Chem. Scand.* **17** (1963) 617.
7. Larsen, F. K., Christensen, A. N. and Rasmussen, S. E. *Acta Chem. Scand.* **21** (1967) 1281.
8. Christensen, A. N. *Acta Chem. Scand.* **24** (1970) 1287.
9. Christensen, A. N. *Acta Chem. Scand.* **19** (1965) 1391.

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