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The Crystal Structure of $NaIn(SiO_3)_2$

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Sodium indium silicate, $NaIn(SiO_3)_2$, was obtained as an impurity by hydrothermal preparation of rhombohedral indium oxide. The crystal structure was determined from three dimensional Patterson and Fourier functions and was refined to a conventional R-value of 4.9 %. The compound has a diopside structure. The space group is $C2/c$, with $a = 9.916$ Å, $b = 9.132$ Å, $c = 5.371$ Å, $\beta = 107.0°$, and the cell contains four formula units.

A hydrothermal investigation of the system In_2O_3—D_2O—Na_2O yielded, in one experiment, the rhombohedral modification of indium oxide which contained as an impurity a few single crystals of a phase of unknown composition. A three-dimensional single crystal X-ray analysis proved that the impurity had the formula $NaIn(SiO_3)_2$.

EXPERIMENTAL

Chemistry. The hydrothermal experiment was performed in a pressure bomb lined with pure gold. Freshly precipitated $In(OD)_3$ was treated with 99.7 % D_2O at 390°C, and 435 atm. for 95 h. The NaOD solution used in the precipitation of In^{3+} was obtained by dissolving Na in D_2O kept in a beaker of pyrex glass. The indium ion solution was prepared by dissolving $In_2(SO_4)_3$ in D_2O. All manipulations with compounds containing deuterium were performed in a glove box under dry nitrogen.

It is assumed that the silicon of the compound $NaIn(SiO_3)_2$ comes from the pyrex glass beaker used in the preparation of NaOD. The amount of the compound in the sample is probably less than 0.1 %.

X-Ray technique. A single crystal of dimensions 0.06 × 0.06 × 0.3 mm³ was investigated by precession methods using Mo$K\alpha$-radiation, $\lambda = 0.7107$ Å. Photographs were taken of 0kl, 1kl, 2kl, 3kl, $h0l$, $h1l$, and $h2l$.

A total of 694 independent hkl reflections were measured with an automatic diffractometer (Arndt-Phillips design)[1] using Mo radiation and balanced filter techniques with a scintillation counter. The usual Lorentz-polarisation corrections were applied, but no absorption correction was made. Only 534 reflections with $I > 2\sigma I$ were used in the structure determination.

STRUCTURE DETERMINATION

Conditions limiting possible reflections *hkl* were $h + k = 2n$. The space group is $C2/c$, No. 15, or Cc, No. 9. A three-dimensional Patterson function $P(u,v,w)$ gave a possible solution with a heavy atom (In) in a special position (0,0.1,0.25) in $C2/c$. The three-dimensional difference Fourier map based on this assumption showed four peaks in general positions, the biggest of these being tetrahedrally surrounded by four of the smaller peaks at distances of 1.6—1.7 Å. The tetrahedra share corners to form infinite chains. From this it was deduced that the central atoms in the tetrahedra were silicon atoms. The difference Fourier map also showed a peak at the special position (0,0.7, 0.25) of height intermediate between that of the silicon peak and those of oxygen. This was assumed to be a sodium atom thus leading to the formula $NaIn(SiO_3)_2$ for the compound.

Refinement proceeded by the method of least squares giving an R-value of 5.5 % at the end of isotropic refinement and 4.9 % after additional anisotropic refinement. A final difference Fourier map showed no significant detail and as all distances and temperature factors are reasonable we assume that the given formula is correct.

CRYSTAL DATA

The formula of the compound is $NaIn(SiO_3)_2$ and the unit cell contains four formula units. Crystal system: monoclinic (b unique), $a = 9.916$ Å, $b = 9.132$ Å, $c = 5.371$ Å, $\beta = 107.0°$. Systematic absences: *hkl*: $h + k \neq 2n$, *h0l*: $l \neq 2n$. Possible space groups: $C2/c$ and Cc; density calculated for four formula units per cell is 4.13 g/cm^3, and the absorption coefficient for Mo-radiation is 56 cm^{-1}, ($\lambda = 0.7107$ Å). The structure factors were calculated using the atomic scattering factors from Vol. III of *International Tables of X-ray Crystallography*, approximated by Bassi polynomials.[2]

Final atomic coordinates and temperature factor parameters are given in Table 1 and interatomic distances and bond angles in Table 2. A list of observed and calculated structure factors is given in Table 3.

Table 1. Atomic coordinates and temperature factors. Diffractometer data, 534 reflections, anisotropic refinement, $R = 4.9$ %.

Atom	x	σx	y	σy	z	σz
Na	0.5	0	0.1966	0.0008	0.25	0
In	0	0	0.1052	0.0001	0.25	0
Si	0.2922	0.0003	0.0869	0.0003	0.7477	0.0005
O_1	0.1194	0.0007	0.0800	0.0007	0.6538	0.0013
O_2	0.1422	0.0008	0.2533	0.0008	0.1851	0.0012
O_3	0.3472	0.0007	0.0112	0.0008	0.5195	0.0011

Table 1. Continued.

Temperature factor parameters with standard deviations ($\times 10^5$).

	b_{11}	σb_{11}	b_{22}	σb_{22}	b_{33}	σb_{33}	b_{12}	σb_{12}	b_{13}	σb_{13}	b_{23}	σb_{23}
Na	627	84	398	79	1328	218	0	0	−545	242	0	0
In	159	8	238	9	866	28	0	0	109	27	0	0
Si	105	26	175	29	534	80	− 56	44	81	79	54	85
O_1	121	69	129	74	827	230	−210	118	−350	219	75	239
O_2	293	77	200	78	650	221	−107	123	139	231	−162	235
O_3	295	71	327	82	111	184	− 48	126	100	211	172	220

Table 2.

Interatomic distances (Å) with standard deviations.

$In-O_1$	2.158	(6)	$Na-O_1$	2.487 (9)
$In-O_1'$	2.211	(7)	$Na-O_2$	2.394 (6)
$In-O_2$	2.056	(8)	$Na-O_3$	2.517 (9)
			$Na-O_3'$	2.922 (9)
$Si-O_1$	1.641	(7)		
$Si-O_2$	1.595	(8)		
$Si-O_3$	1.633	(8)		
$Si-O_3'$	1.664	(7)		

Bond angles (degrees) with standard deviations.

O_1-In-O_1	167.74	(25)	$Si-O_1-In$	121.45 (44)
O_1-In-O_1'	88.82	(25)	$Si-O_1-In'$	122.71 (49)
O_1-In-O_1''	81.78	(25)	$Si-O_1-Na$	114.97 (34)
O_1-In-O_2	92.22	(26)	$In-O_1-In'$	98.20 (45)
O_1-In-O_3'	95.84	(26)	$In-O_1-Na$	88.10 (22)
$O_1'-In-O_1''$	80.15	(28)	$In'-O_1-Na$	105.01 (30)
$O_1'-In-O_2$	91.33	(29)	$Si-O_2-In$	144.89 (44)
$O_1'-In-O_2'$	169.63	(26)	$Si-O_2-Na$	97.53 (35)
O_1-Si-O_2	115.17	(39)	$In-O_2-Na$	93.08 (31)
O_1-Si-O_3	107.51	(37)	$Si-O_3-Si'$	142.24 (40)
O_1-Si-O_3'	107.10	(40)	$Si-O_3-Na$	117.51 (41)
O_2-Si-O_3	110.68	(44)	$Si-O_3-Na'$	103.59 (30)
O_2-Si-O_3'	106.70	(36)	$Si'-O_3-Na$	91.21 (45)
O_3-Si-O_3'	109.55	(40)	$Si'-O_3-Na'$	92.18 (35)
			$Na-O_3-Na'$	110.84 (29)

DISCUSSION

The crystal structure is isostructural to that of diopside reported by Warren and Bragg [3] with indium instead of magnesium and sodium in the place of calcium. The SiO_4 tetrahedra are fairly regular (see Table 2). They form chains along the [001] direction. Indium atoms are octahedrally coordinated; one pair of In—O distances is short (2.06 Å) compared to most other In—O distances (*e.g.* 2.15 Å and 2.20 Å in InOOH,[4] and 2.17 Å in $In(OH)_3$[5]), but is comparable with a short In—O distance (2.07 Å) in rhombohedral In_2O_3.[5] The oxygen atom (O_2) is coordinated to only two other atoms, whereas the

Table 3. Observed and calculated structure factors.

h	k	l	Fo	Fc
0	12	0	536	475
1	13	0	498	-338
0	10	0	1109	1121
1	11	0	323	306
2	12	0	369	-367
0	8	0	375	442
1	9	0	715	688
2	10	0	611	614
3	11	0	571	553
0	6	0	1604	-1623
1	7	0	165	-92
2	8	0	436	438
3	9	0	960	997
4	10	0	951	912
0	4	0	963	-1023
1	5	0	1789	-1801
2	6	0	214	-249
4	8	0	213	185
5	9	0	683	680
6	10	0	702	679
0	2	0	895	871
1	3	0	976	-572
2	4	0	1075	-1048
3	5	0	1405	-1419
4	6	0	657	-639
5	7	0	514	485
6	8	0	569	533
7	9	0	624	612
1	1	0	1158	1146
2	2	0	265	-244
4	4	0	1610	-1599
5	5	0	582	-627
6	6	0	567	-545
7	7	0	454	-471
8	8	0	431	412
2	0	0	1153	1075
3	1	0	1975	1875
4	2	0	196	141
5	3	0	375	-321
6	4	0	590	-594
7	5	0	1737	-1737
8	6	0	567	-530
4	0	0	1017	1048
6	2	0	192	189
7	3	0	497	-488
8	4	0	601	-616
9	5	0	677	-680
10	6	0	811	-814
6	0	0	1917	1830
7	1	0	1214	1210
9	3	0	198	-151
10	4	0	1126	-1132
11	5	0	727	-737
8	0	0	1279	1275
9	1	0	704	691
10	2	0	335	333
11	3	0	240	-243
12	4	0	361	-337
10	0	0	1088	1154
11	1	0	706	681
13	3	0	324	-301
13	1	0	429	405
-13	5	1	309	40
-12	6	1	501	427
-11	7	1	671	617
-10	8	1	319	311
-9	9	1	390	325
-7	11	1	554	-537
-13	3	1	476	-509
-12	4	1	732	-671
-10	6	1	385	407
-9	7	1	788	824
-8	8	1	798	774
-7	9	1	407	-410
-6	10	1	293	-278
-13	1	1	432	-438
-12	2	1	1174	-1164
-11	3	1	795	-835
-8	6	1	653	651
-7	7	1	689	706
-6	8	1	634	651
-5	9	1	616	640
-4	10	1	334	-302
-3	11	1	617	-610
-2	12	1	648	-637
-1	13	1	640	-540
-11	1	1	394	-362
-10	2	1	567	-604
-9	3	1	1257	-1239
-8	4	1	367	-377
-7	5	1	231	240
-6	6	1	608	628
-5	7	1	1471	1465
-4	8	1	652	687
-1	11	1	492	-536
0	12	1	703	-625
-9	1	1	475	-543
-8	2	1	1111	-1147
-6	4	1	325	-298
-4	6	1	471	490
-3	7	1	745	767
-2	8	1	1348	1406
0	10	1	561	-589
1	11	1	446	-422
2	12	1	859	-806
-7	1	1	351	-390
-6	2	1	1213	-1218
-5	3	1	1906	-1892
-4	4	1	423	-457
-3	5	1	462	466
-2	6	1	773	781
-1	7	1	1189	1219
0	8	1	254	284
3	11	1	583	-591
4	12	1	529	-487
-5	1	1	1071	-1052
-4	2	1	1688	-1613
-3	3	1	1808	-1735
-2	4	1	935	-939
0	6	1	656	659
1	7	1	1410	1427
2	8	1	1017	1036
5	11	1	423	-424
-2	2	1	2523	-2568
-1	3	1	1664	-1668
0	4	1	449	450
2	6	1	624	645
3	7	1	789	791
4	8	1	712	736
5	9	1	601	655
-1	1	1	973	+998
0	2	1	665	-694
1	3	1	816	-859
2	4	1	737	-750
3	5	1	483	519
4	6	1	561	563
5	7	1	1121	1162
6	8	1	789	831
1	11	1	1021	-1008
2	12	1	2082	-2098
3	3	1	1761	-1743
6	6	1	530	600
7	7	1	709	778
8	8	1	630	642
4	2	1	1306	-1361
5	3	1	2229	-2238
6	4	1	455	-443
7	5	1	226	191
8	6	1	463	524
9	7	1	905	901
5	1	1	868	-864
6	2	1	1315	-1357
7	3	1	343	-363
8	4	1	441	-463
10	6	1	399	423
7	1	1	395	-425
8	2	1	1133	-1145
9	3	1	870	-924
9	1	1	521	-560
10	2	1	362	-425
11	3	1	628	-700
12	4	1	545	-525
13	5	2	624	621
9	0	2	521	-506
8	10	2	606	-560
-7	11	2	749	-680
-12	4	2	335	376
-11	5	2	740	736
-10	6	2	526	514
-8	8	2	401	-373
-7	9	2	750	-755
-6	10	2	526	-534
-13	1	2	660	-695
-12	2	2	257	177
-11	3	2	266	313
-10	4	2	847	878
-9	5	2	695	732
-8	6	2	377	374
-7	7	2	334	334
-6	8	2	317	-292
-5	9	2	648	-637
-4	10	2	924	+923
-3	11	2	318	-367
-2	12	2	468	462
-12	0	2	435	-327
-11	1	2	544	-552
-10	2	2	519	-524
-9	3	2	560	408
-8	4	2	740	727
-7	5	2	1522	1510
-6	6	2	1065	1076
-5	7	2	421	-365
-4	8	2	408	-386
-3	9	2	708	-747
-2	10	2	667	-686
-1	11	2	271	-229
-10	0	2	1251	-1249
-9	1	2	302	-302
-7	3	2	201	170
-6	4	2	967	980
-5	5	2	732	716
-4	6	2	602	595
-3	7	2	262	278
-2	8	2	506	-536
-1	9	2	792	-809
0	10	2	879	-878
1	11	2	358	-406
-8	0	2	987	-1000
-7	1	2	1686	-1668
-6	2	2	224	214
-4	4	2	1026	1043
-3	5	2	1686	1734
-2	6	2	291	-311
-1	7	2	223	-273
1	9	2	731	-757
2	10	2	519	-535
3	11	2	503	-493
-6	0	2	1699	-1678
-5	1	2	596	-587
-4	2	2	558	-509
-3	3	2	758	731
-2	4	2	756	740
-1	5	2	1027	1052
0	6	2	1546	1628
2	8	2	500	-489
3	9	2	678	-671
4	10	2	925	-989
-4	0	2	2007	-1907
-3	1	2	766	-783
-2	2	2	207	-233
-1	3	2	187	199
0	4	2	1528	1559
1	5	2	1258	1267
2	6	2	475	481
3	7	2	410	434
4	8	2	301	-281
5	9	2	558	-628
6	10	2	518	-554
-2	0	2	633	-663
-1	1	2	909	-932
0	2	2	122	144
2	4	2	634	637
3	5	2	1807	1858
4	6	2	436	432
5	7	2	405	-402
6	8	2	254	-319
7	9	2	720	-716
0	0	2	2675	-2636
1	1	2	1614	-1531
3	3	2	583	552
4	4	2	1082	1069
5	5	2	566	554
6	6	2	389	434
8	8	2	362	-399
2	0	2	1796	-1697
3	1	2	1230	-1185
4	2	2	690	-697
5	3	2	271	304
6	4	2	814	863
7	5	2	1078	1099
8	6	2	433	452
4	0	2	1814	-1704
5	1	2	185	-151
8	4	2	500	509
9	5	2	643	697
10	6	2	668	670
6	0	2	876	-823
7	1	2	1188	-1176
9	3	2	245	263
10	4	2	668	744
8	0	2	1857	-889
9	1	2	404	-410
10	2	2	455	-476
10	0	2	1346	-1363
11	1	2	566	-608
-12	6	3	490	-487
-11	7	3	554	-581
-10	8	3	487	-592
-9	9	3	555	-498
-14	2	3	521	513
-13	3	3	374	344
-12	4	3	623	544
-10	*6	3	332	-435
-9	7	3	797	-805
-8	8	3	713	-708
-6	10	3	343	292
-13	1	3	304	375
-12	2	3	962	1014
-11	3	3	696	747
-8	6	3	405	-470
-7	7	3	692	-643
-6	8	3	567	-530
-3	11	3	603	568
-2	12	3	613	641
-11	1	3	412	451
-10	2	3	642	611
-9	3	3	1309	1338
-8	4	3	596	586
-7	5	3	299	-347
-6	6	3	617	-609
-5	7	3	1192	-1206
-4	8	3	577	-600
-1	11	3	472	347
-9	1	3	515	530
-8	2	3	1229	1245
-7	3	3	262	270
-4	6	3	553	-626
-3	7	3	665	-678
-2	8	3	1123	-1153
-1	9	3	532	-518
0	10	3	478	440
1	11	3	443	407
-7	1	3	260	254
-6	2	3	907	923
-5	3	3	1284	1317
-3	5	3	394	-386
-2	6	3	554	-544
-1	7	3	1048	-1115
0	8	3	400	-342
-5	1	3	992	993
-4	2	3	927	976
-3	3	3	1066	1108
-2	4	3	949	981
0	6	3	386	-469
1	7	3	1103	-1110
2	8	3	960	-968
3	9	3	329	250
4	10	3	299	357
-3	1	3	200	190
-2	2	3	2078	2103
-1	3	3	1689	1702
2	6	3	687	-718
3	7	3	711	-644
4	8	3	357	-419
5	9	3	582	-621
-1	1	3	580	590
0	2	3	872	867
1	3	3	971	950
2	4	3	495	467
3	5	3	306	-309
4	6	3	411	-459
5	7	3	984	-977
6	8	3	599	+644
1	1	3	936	814
2	2	3	1517	1435
3	3	3	492	507
6	6	3	366	-402
7	7	3	637	-593
3	1	3	245	222
4	2	3	791	808
5	3	3	1561	1576
6	4	3	447	448
8	6	3	496	-482
5	1	3	526	538
6	2	3	1126	1121
7	3	3	565	524
7	1	3	360	323
8	2	3	999	1015
9	3	3	787	814
9	1	3	595	587
-9	9	4	302	561
-12	4	4	278	-208
-11	5	4	662	-682
-10	6	4	706	-653
-9	7	4	288	282
-8	8	4	334	318
-7	9	4	599	584
-13	1	4	563	546
-10	4	4	956	-885
-9	5	4	336	-346
-7	7	4	317	-353
-6	8	4	409	427
-5	9	4	398	456
-4	10	4	678	642
-3	11	4	467	508
-12	0	4	587	581
-11	1	4	582	566
-8	4	4	671	-691
-7	5	4	1456	-1352
-6	6	4	617	-615
-5	9	4	807	751
-2	10	4	534	477
-10	0	4	1010	933
-9	1	4	425	434
-7	3	4	428	-415
-6	4	4	582	-544
-5	5	4	772	-778
-4	6	4	917	-927
-2	8	4	291	276
-1	9	4	572	635
0	10	4	915	876
-8	0	4	479	461
-7	1	4	971	998
-6	2	4	320	295
-5	3	4	306	-334
-4	4	4	941	-958
-3	5	4	1161	-1153
0	8	4	382	349
1	9	4	562	500
2	10	4	417	365
-6	0	4	1696	1626
-5	1	4	412	362
-4	2	4	153	127
-2	4	4	769	-850
-1	5	4	744	-767
0	6	4	646	-688
2	8	4	477	479
3	9	4	645	629
-4	0	4	1747	1588
-3	1	4	1393	1370
-1	3	4	307	-312
0	4	4	856	-863
1	5	4	997	-1048
2	6	4	327	-351
-2	0	4	109	228
-1	1	4	400	418
0	2	4	509	485
1	3	4	377	-419
2	4	4	355	-382
3	5	4	1174	-1199
4	6	4	855	-890
0	0	4	1854	1810
1	1	4	483	435
2	2	4	198	-181
4	4	4	1046	-1066
5	5	4	512	-475
2	0	4	1117	1051
3	1	4	1297	1255
4	2	4	241	187
6	4	4	618	-614
7	5	4	970	-982
4	0	4	1238	1188
5	1	4	373	376
7	3	4	453	-364
6	0	4	817	774
7	1	4	645	602
8	0	4	633	626
9	1	4	411	274
-10	6	5	317	336
-9	7	5	746	669
-8	8	5	844	-735
-12	2	5	819	-778
-11	3	5	441	-418
-9	5	5	235	61
-8	6	5	444	455
-7	7	5	374	374
-6	8	5	470	474
-11	1	5	458	-391
-10	2	5	526	-451
-9	3	5	1112	+1062
-8	4	5	538	-512
-6	6	5	482	475
-5	7	5	1086	1013
-4	8	5	319	268
-9	1	5	481	-478
-8	2	5	1092	-1037
-7	3	5	558	-501
-6	4	5	213	-224
-4	6	5	429	408
-3	7	5	606	578
-2	8	5	905	860
-1	9	5	347	338
-6	2	5	797	-763
-5	3	5	955	-931
-3	5	5	242	311
-2	6	5	530	528
-1	7	5	666	652
0	8	5	410	396
-5	1	5	689	-751
-4	2	5	686	-634
-3	3	5	411	-406
-2	4	5	521	-559
0	6	5	389	407
1	7	5	888	850
2	8	5	695	685
-3	1	5	1188	-212
-2	2	5	1261	-1256
-1	3	5	1264	-1281
2	6	5	377	424
3	7	5	608	624
-1	1	5	438	-410
0	2	5	675	-630
1	3	5	934	-899
2	4	5	562	-578
4	6	5	389	388
1	1	5	591	-553
2	2	5	1239	-1176
3	3	5	255	-265
5	5	5	310	74
3	1	5	276	-291
4	2	5	500	-472
5	3	5	1023	-979
5	1	5	418	-386
6	2	5	743	-665
-10	4	6	495	529
-9	5	6	498	460
-11	1	6	408	-533
-9	3	6	415	373
-8	4	6	396	425
-7	5	6	779	778
-6	6	6	465	494
-10	0	6	876	-1003
-7	3	6	232	209
-6	4	6	663	679
-5	5	6	335	343
-4	6	6	671	679
-3	7	6	304	346
-8	0	6	329	-370
-7	1	6	804	-777
-4	4	6	607	570
-3	5	6	1120	1116
-6	0	6	639	-635
-5	1	6	361	-380
-3	3	6	318	352
-2	4	6	433	362
-1	5	6	553	565
0	6	6	587	577
-4	0	6	984	-1207
-3	1	6	660	-749
-2	2	6	162	-197
-1	3	6	174	230
0	4	6	938	889
1	5	6	443	411
-2	0	6	630	-634
-1	1	6	413	-380
0	2	6	220	-193
2	4	6	365	300
0	0	6	912	-859
1	1	6	515	-515
2	2	6	246	211
3	3	6	243	255
2	0	6	471	-421
3	1	6	629	-592
4	2	6	436	-291

other oxygen atoms are four coordinated. O_1 is coordinated with two indium atoms, one silicon, and one sodium atom. O_3 is coordinated with two silicon atoms and two sodium atoms. O_2 is coordinated with one indium, one silicon, and one sodium atom, and these three distances are significantly shorter than the corresponding distances from O_1 and O_3. The sodium atoms are eight coordinated although two of the surrounding oxygen atoms are much further away than the others. The coordination is best described as a very distorted tetragonal antiprism.

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