Table 5. *Torsional angles in the rings**

Ring *A*		Ring *B*		Ring *C*		Ring *D*		Ring *E*	
Bond	φ_{A-B}	Bond	φ_{A-B}	Bond	φ_{A-B}	Bond	φ_{A-B}	Bond	φ_{A-B}
1—2	55·6°	5—6	58·1°	8—9	51·8°	13–14	46·3°	N–22	60·3°
2—3	50·1	6—7	58·8	9–11	49·8	14–15	34·7	22–23	53·1
3—4	55·2	7—8	57·0	11–12	54·3	15–16	9·9	23–24	49·8
4—5	62·8	8—9	56·4	12–13	55·7	16–17	18·5	24–25	54·0
5–10	60·6	9–10	54·0	13–14	62·7	17–13	39·2	25–26	59·6
10—1	57·7	10—5	54·6	14—8	62·7			26–N	63·0

* φ_{A-B} is the torsional angle about the *A*-*B* bond, in which the other two atoms required to define the bond are those attached to either end of the bond and are in the ring in question.

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The Crystal Structure of Hexabarium 17-Titanate

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(*Received* 20 *October* 1969)

The crystal structure and the chemical composition of $Ba_6Ti_{17}O_{40}$, a new compound in the system $BaO–TiO_2$, have been established by single-crystal methods. Hexabarium 17-titanate crystallizes in space group $C2/c$ with $a=9·883$, $b=17·08$, $c=18·92$ Å, $\beta=98°42'$, $Z=4$. The 2094 observed F_{hkl} were used in a combination of Patterson and Fourier methods to determine the crystal structure and to refine it to $R=0·06$. The structure can be described as a three-dimensional framework of TiO_6 coordination octahedra. The most prominent features of this framework are ribbons of octahedra of composition Ti_3O_{10} which extend in the $[\bar{1}10]$ direction at height $z=0$, and in the [110] direction at $z=\frac{1}{2}$. The ribbons are joined by clusters of octahedra of composition $Ti_{11}O_{40}$. The voids in this framework are filled by the Ba atoms. An alternate way of looking at the crystal structure is to regard it as a hexagonally close-packed array of oxygen and barium atoms with the titanium atoms filling the energetically most favorable octahedral voids. The direction of packing is [103] and the stacking sequence is *ABCACABCBCABABCACABCBCAB*. $Ba_6Ti_{17}O_{40}$ is another example in the short list of titanates which can be described as close-packed arrays, while most belong to the Wadsley–Anderson type phases with one cell edge of about 4 Å. The details of the atomic arrangement show appreciable distortions of the bond lengths and angles. The individual bond distances Ti–O vary from 1·77 to 2·43 Å. The mean of all Ti–O bond lengths formed by one oxygen atom can be predicted by using the expression $d_{\text{Ti–O}}=(1·552+0·200\zeta)$ Å, where ζ is the sum of the electrostatic valences received by this oxygen atom. This is in accord with the extended electrostatic valence rule.

Introduction

Compounds in the system $BaO–TiO_2$ have been extensively studied in recent years. So far the crystal structures of Ba_2TiO_4 (Bland, 1961), cubic $BaTiO_3$ (Megaw, 1947), hexagonal $BaTiO_3$ (Burbank & Evans, 1948), $BaTi_2O_5$ (Harrison, 1956), $BaTi_4O_9$ (Lukaszewicz, 1957) and $BaTi_5O_{11}$ (Tillmanns, 1969) have been described. Rase & Roy (1955) report another compound in this system of composition $BaTi_3O_7$ and two more are mentioned by Kwestroo (1960): $Ba_2Ti_5O_{12}$ and $Ba_2Ti_9O_{20}$. The X-ray powder patterns for these three compounds are not indexed and single-crystal work has not been undertaken.

The crystal structures differ considerably. Ba_2TiO_4 has an unusual tetrahedral coordination of oxygen atoms around titanium atoms. $BaTi_5O_{11}$ and both modifications of $BaTiO_3$ contain close-packed layers of barium and oxygen atoms with titanium atoms in octahedral voids. TiO_6-octahedra share only corners in the cubic

Table 1. *Observed and calculated structure factors for* $Ba_6Ti_{17}O_{40}$

H	K	L	FO	FC
0	0	2	58	37
0	0	4	28	-4
0	0	6	322	319
0	0	8	421	-400
0	0	12	88	109
0	0	14	108	-113
0	0	16	697	693
0	0	22	198	182
0	2	0	77	-56
0	2	1	156	-107
0	2	2	141	108
0	2	3	35	-38
0	2	4	32	32
0	2	5	109	-102
0	2	6	56	-57
0	2	7	189	-190
0	2	8	38	-35
0	2	9	73	71
0	2	10	169	-170
0	2	11	227	223
0	2	13	72	81
0	2	14	53	53
0	2	15	92	90
0	2	16	69	-72
0	2	17	54	54
0	2	18	71	66
0	4	0	77	-75
0	4	1	370	-355
0	4	2	112	-116
0	4	3	56	-58
0	4	4	66	65
0	4	5	112	112
0	4	6	80	88
0	4	7	327	-316
0	4	9	251	241
0	4	10	170	170
0	4	11	80	89
0	4	12	55	58
0	4	13	35	-30
0	4	14	44	-40
0	4	15	302	291
0	4	18	71	-73
0	4	19	64	-62
0	4	21	90	96
0	6	0	497	-517
0	6	1	175	176
0	6	2	54	60
0	6	3	23	-17
0	6	4	54	51
0	6	6	67	-64
0	6	7	66	68
0	6	8	107	108
0	6	9	32	17
0	6	10	266	263
0	6	14	119	116
0	6	15	109	-105
0	6	16	218	-209
0	6	17	104	56
0	6	19	51	-44
0	8	0	162	-170
0	8	1	35	39
0	8	3	156	165
0	8	5	91	101
0	8	6	126	-134
0	8	7	77	-78
0	8	8	139	145
0	8	9	104	109
0	8	11	156	-154
0	8	12	49	-50
0	8	13	120	-130
0	8	14	84	82
0	8	15	83	-78
0	8	16	64	-63
0	8	17	90	-96
0	8	19	44	37
0	8	20	53	47
0	8	21	62	56
0	10	0	120	134
0	10	1	150	167
0	10	2	65	70
0	10	4	57	61
0	10	5	46	-46
0	10	6	50	52
0	10	7	295	307
0	10	8	198	-205
0	10	9	243	-247
0	10	10	75	-76
0	10	11	80	-67
0	10	13	61	54
0	10	14	50	48
0	10	15	187	-191
0	10	16	54	-54
0	10	20	89	75
0	12	0	578	593
0	12	1	213	-217
0	12	2	230	236
0	12	3	72	-78
0	12	5	38	-39
0	12	10	98	-94
0	12	13	100	84
0	12	14	97	92
0	12	15	98	96
0	12	16	276	276
0	12	17	133	-138
0	12	18	166	167
0	14	0	107	122
0	14	2	119	-130
0	14	3	40	-32
0	14	4	45	-42
0	14	5	127	-129
0	14	6	168	181
0	14	7	49	-49
0	14	8	211	-220
0	14	10	85	90
0	14	11	147	149
0	14	12	61	54
0	14	13	90	94
0	14	14	168	-176
0	14	15	55	44
0	14	16	72	52
0	16	0	89	-121
0	16	1	37	-43
0	16	4	57	66
0	16	7	84	-96
0	16	8	202	213
0	16	9	112	113
0	16	10	46	51
0	16	11	51	47
0	16	12	93	96
0	18	0	68	-65
0	18	1	61	-72
0	18	2	105	-102
0	18	3	102	107
0	18	5	106	117
0	18	7	111	-120
0	18	9	178	186
0	18	10	98	97
0	18	11	53	-55
0	20	0	87	-79
0	20	1	83	104
0	20	2	47	51
0	20	3	48	42
0	20	6	147	-160
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1	1	-21	95	-102
1	1	-18	47	-53
1	1	-17	62	58
1	1	-16	125	114
1	1	-15	47	-45
1	1	-13	60	-62
1	1	-12	231	-224
1	1	-11	157	-150
1	1	-10	34	-32
1	1	-9	92	-90
1	1	-8	68	-66
1	1	-7	124	128
1	1	-6	639	-564
1	1	-5	156	-153
1	1	-4	46	47
1	1	-2	22	21
1	1	0	42	32
1	1	2	38	45
1	1	3	107	-92
1	1	5	266	-254
1	1	6	50	-44
1	1	7	135	-128
1	1	8	34	29
1	1	9	86	87
1	1	10	323	-318
1	1	11	59	-63
1	1	13	81	84
1	1	14	52	36
1	1	16	68	-59
1	1	18	88	82
1	1	20	144	138
1	1	21	114	-106
1	1	22	76	-66
1	3	-22	65	75
1	3	-21	252	237
1	3	-19	56	-56
1	3	-17	110	109
1	3	-13	305	-314
1	3	-12	108	107
1	3	-11	73	73
1	3	-9	82	-78
1	3	-8	34	-41
1	3	-7	266	-260
1	3	-6	138	140
1	3	-5	523	502
1	3	-4	68	62
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1	3	1	190	199
1	3	2	37	-35
1	3	3	317	-332
1	3	4	151	151
1	3	5	116	-106
1	3	7	37	-34
1	3	8	40	-41
1	3	9	343	-350
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1	3	11	273	280
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1	3	13	69	77
1	3	14	61	62
1	3	15	48	-46
1	3	17	236	232
1	3	18	60	-60
1	3	20	71	67
1	3	21	112	-101
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1	5	-16	236	-224
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1	5	-13	244	-233
1	5	-12	73	-69
1	5	-9	99	-105
1	5	-8	87	88
1	5	-7	51	-42
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1	5	-5	114	-118
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1	5	-2	218	-217
1	5	0	275	-273
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1	5	3	403	-382
1	5	4	346	-327
1	5	5	45	-54
1	5	6	55	-64
1	5	7	59	59
1	5	8	63	63
1	5	9	49	-41
1	5	10	80	88
1	5	11	206	-208
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1	5	13	62	65
1	5	14	115	-122
1	5	15	43	-24
1	5	16	105	-102
1	5	18	83	-84
1	5	19	99	-92
1	5	20	252	-245
1	5	21	59	-56
1	7	-20	173	-152
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1	7	-18	84	80
1	7	-17	86	-83
1	7	-16	49	-56
1	7	-15	72	76
1	7	-14	150	-148
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1	7	-12	197	191
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1	7	-10	101	-95
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1	7	-6	429	439
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1	7	-3	85	-86
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1	7	4	25	-11
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1	7	6	83	-81
1	7	7	84	87
1	7	8	137	-146
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1	7	12	201	-195
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1	7	15	68	-61
1	7	16	117	117
1	7	18	239	-231
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1	7	20	117	-127
1	7	21	106	101
1	9	-20	45	48
1	9	-18	43	37
1	9	-17	101	-104
1	9	-15	82	93
1	9	-14	122	120
1	9	-13	119	112
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1	9	-7	110	114
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1	9	-3	66	-65
1	9	-2	52	48
1	9	-1	58	-65
1	9	0	33	-23
1	9	1	33	-34
1	9	2	100	106
1	9	3	96	107
1	9	4	62	53
1	9	5	117	122
1	9	6	64	61
1	9	7	49	54
1	9	8	66	-68
1	9	9	170	187
1	9	10	97	-109
1	9	11	99	-94
1	9	12	64	79
1	9	13	119	-116
1	9	15	49	-53
1	9	16	47	-41
1	9	17	113	-113
1	9	18	85	87
1	9	19	44	-49
1	11	-19	196	186
1	11	-16	85	81
1	11	-15	197	-188
1	11	-14	73	-70
1	11	-13	255	259
1	11	-12	43	-47
1	11	-11	70	-69
1	11	-10	93	-86
1	11	-9	48	58
1	11	-8	184	-182
1	11	-7	49	49
1	11	-6	194	-193
1	11	-5	32	-41
1	11	-4	168	-169
1	11	-3	221	234
1	11	-1	101	110
1	11	0	62	60
1	11	1	338	-355
1	11	3	406	417
1	11	4	106	102
1	11	6	35	-28
1	11	7	71	-87
1	11	8	150	-156
1	11	9	162	164
1	11	10	106	-116
1	11	11	45	-37
1	11	12	106	-110
1	11	15	134	144
1	11	17	193	-179
1	13	-14	53	54
1	13	-13	180	-183
1	13	-12	190	-194
1	13	-11	66	-58
1	13	-10	44	42
1	13	-7	84	-89
1	13	-6	253	-272
1	13	-5	156	173
1	13	-2	50	59
1	13	0	51	-46
1	13	2	160	178
1	13	3	140	-153
1	13	4	90	-99
1	13	5	118	-117
1	13	7	71	-72
1	13	8	110	115
1	13	9	82	-84
1	13	10	151	-159
1	13	11	143	148
1	13	14	99	101
1	13	16	81	-65
1	13	17	97	96
1	15	-16	83	-72
1	15	-15	68	-96
1	15	-11	92	-98
1	15	-10	51	54
1	15	-9	62	-57
1	15	-8	51	44
1	15	-5	69	73
1	15	-4	118	124
1	15	-3	44	37
1	15	-2	72	-75
1	15	0	127	-133
1	15	2	49	63
1	15	4	42	-37
1	15	5	148	-152
1	15	7	62	-66
1	15	8	107	118
1	15	12	75	65
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1	15	14	64	70
1	17	-13	241	-251
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1	17	-7	96	-108
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1	17	-2	103	-113
1	17	-1	46	-45
1	17	0	83	-95
1	17	1	183	182
1	17	2	185	-188
1	17	3	355	-357
1	17	4	42	-29
1	17	5	60	68
1	17	6	56	-37
1	17	7	155	155
1	17	9	139	-145
1	17	10	49	39
1	17	11	55	-60
1	19	-9	60	60
1	19	-8	102	119
1	19	-7	71	69
1	19	-5	50	-50
1	19	-3	50	-60
1	19	-1	53	-52
1	19	3	76	89
1	19	5	64	81
1	19	6	59	-46
1	19	7	114	110
2	0	-22	193	-179
2	0	-18	303	286
2	0	-16	56	-52
2	0	-12	398	394
2	0	-10	375	-374
2	0	-6	182	-174
2	0	-4	139	-149
2	0	-2	93	101
2	0	2	56	-51
2	0	4	652	665
2	0	6	303	-298
2	0	8	62	-63
2	0	10	179	170
2	0	12	252	-240
2	0	14	190	-181
2	0	16	176	167
2	0	20	301	289
2	2	-22	59	-63
2	2	-21	110	115
2	2	-20	49	59
2	2	-19	114	108
2	2	-15	82	79
2	2	-14	94	93
2	2	-12	31	-25
2	2	-11	177	-171
2	2	-10	31	33
2	2	-9	33	-32
2	2	-8	69	-73
2	2	-7	29	-33
2	2	-6	117	-113
2	2	-5	77	81
2	2	-4	44	38
2	2	-3	131	136
2	2	-2	76	-72
2	2	-1	37	39
2	2	0	40	41
2	2	1	57	66
2	2	2	86	91
2	2	3	61	65
2	2	5	273	-265
2	2	6	89	90
2	2	7	226	-226
2	2	8	74	-71
2	2	9	44	-42
2	2	10	43	-38
2	2	11	109	-106
2	2	14	89	-91
2	2	15	88	83
2	2	16	64	66
2	2	17	45	-37
2	2	18	55	53
2	2	19	49	39
2	4	-22	115	110
2	4	-21	69	64
2	4	-19	299	295
2	4	-18	60	-66
2	4	-17	79	-73
2	4	-16	115	-112
2	4	-15	41	53
2	4	-14	54	-55
2	4	-13	65	65
2	4	-12	38	39
2	4	-11	191	-186
2	4	-10	79	-75
2	4	-9	136	139
2	4	-8	88	90
2	4	-7	42	-41
2	4	-6	179	181
2	4	-5	127	-114
2	4	-4	56	57
2	4	-3	583	540
2	4	-2	33	34
2	4	-1	33	-36
2	4	0	105	-116
2	4	1	31	-39
2	4	2	105	-114
2	4	3	183	183
2	4	5	273	-281
2	4	6	74	-84
2	4	10	64	68
2	4	11	276	-272
2	4	12	73	79
2	4	13	241	234
2	4	14	124	120
2	4	15	75	78
2	4	16	88	-85
2	4	17	77	-70
2	4	18	92	-103
2	4	19	112	101
2	4	21	75	-78
2	6	-22	206	208
2	6	-20	93	81
2	6	-19	83	-81
2	6	-18	107	-93
2	6	-17	45	38
2	6	-16	97	112
2	6	-14	49	-59
2	6	-13	141	-131
2	6	-12	422	-423
2	6	-11	247	240
2	6	-10	518	529
2	6	-8	395	371
2	6	-6	364	370
2	6	-4	516	511
2	6	-3	147	-147
2	6	0	100	107
2	6	1	45	-41
2	6	3	176	-189
2	6	4	671	-732
2	6	5	315	314
2	6	6	465	483
2	6	7	75	-74
2	6	8	375	409
2	6	10	125	115
2	6	11	54	51
2	6	12	354	341
2	6	13	85	-85
2	6	14	185	184
2	6	19	77	-92
2	6	20	259	-248
2	8	-21	180	-175
2	8	-19	93	-99
2	8	-18	128	-122
2	8	-17	130	-119
2	8	-16	39	25
2	8	-15	41	41
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Table 1 (*cont.*)

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9	1	-12	70	-60
9	1	-11	46	44
9	1	-10	77	71
9	1	-9	79	70
9	1	-4	200	200
9	1	-2	113	-109
9	1	-1	130	-127
9	1	0	47	-40
9	1	4	76	-71
9	1	7	77	94
9	1	8	65	62
9	1	12	164	151
9	3	-17	87	83
9	3	-15	70	-64
9	3	-14	43	24
9	3	-11	234	219
9	3	-10	86	-102
9	3	-9	102	-105
9	3	-5	107	109
9	3	-4	77	-65
9	3	-3	344	-333
9	3	0	52	-48
9	3	3	116	-95
9	3	5	137	143
9	3	6	52	-94
9	3	11	149	155
9	5	-16	102	93
9	5	-15	103	-54
9	5	-14	135	130
9	5	-13	66	-57
9	5	-11	118	111
9	5	-9	81	-86
9	5	-8	90	-92
9	5	-7	103	-115
9	5	-6	74	-81
9	5	-5	66	-66
9	5	-4	138	-133
9	5	-1	158	-164
9	5	0	123	123
9	5	1	61	-75
9	5	2	50	45
9	5	3	50	-91
9	5	5	60	65
9	5	6	83	76
9	5	8	113	-120
9	5	9	128	-130
9	5	10	106	-109
9	7	-15	124	119
9	7	-12	147	135
9	7	-11	65	-67
9	7	-10	165	-153
9	7	-7	100	95
9	7	-6	46	-42
9	7	-5	61	45
9	7	-4	294	-312
9	7	-3	50	98
9	7	-2	223	231
9	7	-1	188	174
9	7	1	115	122
9	7	2	100	-104
9	7	4	168	167
9	7	6	97	-88
9	7	8	77	-74
9	7	9	55	53
9	9	-13	79	-75
9	9	-11	122	-123
9	9	-5	67	-63
9	9	-3	156	158
9	9	-2	90	-92
9	9	-1	80	87
9	9	0	48	-39
9	9	2	64	-48
9	9	4	72	-60
9	9	5	66	-75
9	9	7	95	-108
9	9	8	82	-91
9	11	-11	186	-188
9	11	-9	103	115
9	11	-6	58	53
9	11	-5	45	-45
9	11	-4	65	62
9	11	-3	103	105
9	11	-2	49	44
9	11	0	76	-82
9	11	2	70	-64
9	11	3	215	225
9	11	5	194	-195
9	11	6	80	-80
9	13	-5	51	40
9	13	-4	99	101
9	13	-3	131	-127
9	13	-2	72	-90
9	13	2	56	47
10	0	-12	72	-66
10	0	-10	273	-264
10	0	-8	253	246
10	0	-6	49	-55
10	0	-2	99	82
10	0	0	87	-92
10	0	2	146	-132
10	0	4	73	-75
10	0	6	314	-320
10	0	8	191	173
10	2	-9	121	115
10	2	-7	67	58
10	2	-6	105	106
10	2	-5	51	-44
10	2	-4	50	59
10	2	-3	110	-113
10	2	-1	132	-131
10	2	0	52	46
10	2	1	49	-58
10	2	5	97	-95
10	2	7	80	65
10	2	9	91	93
10	4	-14	125	109
10	4	-13	81	70
10	4	-9	209	187
10	4	-8	59	54
10	4	-6	64	-64
10	4	-5	55	40
10	4	-4	50	-44
10	4	-3	86	86
10	4	-1	247	-234
10	4	1	65	72
10	4	2	89	108
10	4	3	57	52
10	4	4	65	62
10	4	5	85	-76
10	4	7	164	170
10	4	8	68	55
10	6	-12	93	96
10	6	-10	311	307
10	6	-9	138	-147
10	6	-8	270	-256
10	6	-6	112	-110
10	6	-1	48	41
10	6	0	138	138
10	6	1	57	-45
10	6	2	143	145
10	6	4	85	77
10	6	6	299	304
10	6	7	146	-147
10	6	8	165	-151
10	8	-11	82	-75
10	8	-10	60	54
10	8	-7	91	-86
10	8	-6	73	60
10	8	-4	79	59
10	8	-3	90	77
10	8	-2	79	-71
10	8	0	96	88
10	8	1	106	100
10	8	2	59	57
10	8	5	51	-40
10	8	6	61	57
10	10	-9	165	-151
10	10	-8	51	53
10	10	-7	93	86
10	10	-6	98	99
10	10	-4	98	92
10	10	-2	67	48
10	10	-1	258	253
10	10	0	81	-81
10	10	1	60	-60
11	1	-11	88	71
11	1	-9	147	152
11	1	-7	119	109
11	1	-6	110	103
11	1	-5	73	65
11	1	0	141	131
11	1	1	115	112
11	1	2	246	-238
11	1	3	112	-99
11	1	4	81	-90
11	1	5	68	68
11	3	-9	60	67
11	3	-7	194	192
11	3	-5	91	-98
11	3	-2	96	-80
11	3	-1	50	80
11	3	0	79	-63
11	3	1	269	-257
11	3	4	51	-40
11	3	5	68	58
11	5	-10	60	60
11	5	-9	60	-45
11	5	-7	158	147
11	5	-4	86	-78
11	5	3	68	-62
11	5	4	120	113
11	7	-8	69	42
11	7	-7	68	-63
11	7	-6	170	-165
11	7	0	150	-153
11	7	1	88	77
11	7	2	165	165
12	0	-4	443	442
12	0	-2	76	83

modification of $BaTiO_3$ while there are common corners and a shared face in the hexagonal modification and common corners and edges in $BaTi_5O_{11}$. In $BaTi_2O_5$ and $BaTi_4O_9$, as in many alkali titanates, coordination octahedra around Ti share edges to form infinite chains parallel to a short cell edge of about 4 Å (this distance corresponds to the height of one TiO_6 octahedron). Accordingly crystals grow as needles in the direction of the chains, while hexagonal $BaTiO_3$ and $BaTi_5O_{11}$ grow as plates parallel to the close-packed layers. The morphology and preliminary X-ray investigations of $Ba_6Ti_{17}O_{40}$, a new compound in this system, revealed some similarities to the latter compounds and it appeared of interest to determine its crystal structure.

Experimental

Material of composition $BaO:TiO_2=1:3$ was heated on a platinum plate to 1400°C and quenched. The matrix contained a large number of single crystals most of which were $BaTi_4O_9$. A few crystals showed X-ray patterns which could not be assigned to any of the known compounds in the system $BaO–TiO_2$.

A microprobe analysis was then carried out using single crystals of $BaTi_4O_9$ and $BaTi_5O_{11}$ as standards. The result showed a molar ratio of $Ba:Ti=1:2{\cdot}82$ as compared with $BaTi_4O_9$ and $1:2{\cdot}84$ as compared with $BaTi_5O_{11}$. From the total number of measurements a statistical error of about 1·5% was estimated; systematic errors seemed to be negligible since standards very close in chemical composition to the sample had been used.

There remained still some uncertainty about the chemical formula as the rather large volume of the unit cell of 3156 $Å^3$ made several combinations possible. Unfortunately we were not able to measure the density because of the few and small crystals available. Assuming a value around 4 or 5 $g.cm^{-3}$ from comparison with other barium titanates and taking into account the number of equivalent positions in space groups *Cc* and *C*2/*c* the following combinations seemed most likely:

$$Ba_5Ti_{14}O_{33},\ Ba:Ti=1:2{\cdot}8,\quad Z=4,\ D_x=3{\cdot}95\ g.cm^{-3}$$
$$Ba_6Ti_{17}O_{40},\ Ba:Ti=1:2{\cdot}83,\ Z=4,\ D_x=4{\cdot}80$$
$$Ba_7Ti_{20}O_{47},\ Ba:Ti=1:2{\cdot}86,\ Z=4,\ D_x=5{\cdot}63\,.$$

The crystal used for intensity data collection was a fraction of a larger one and was of irregular shape with minimum and maximum diameters of 0·09 and 0·15 mm respectively and a mass of approximately 4 μg. There was a thin protuberance on the crystal in the direction of the maximum diameter. With a linear absorption coefficient of 61·3 cm^{-1} for Ag $K\alpha$ radiation there could be a maximum error of 30% in F^2 for this direction as compared with the minimum path. However, owing to the way the crystal was mounted, this particular orientation was never reached. The observed variation in F^2 for measurements of equivalent intense reflections exceeded 10% in only one case (11·5%). Therefore an absorption correction did not seem necessary.

The crystal was mounted on a eucentric goniometer head and data were collected on a four-circle automatic diffractometer following generally the methods described by Corfield, Doedens & Ibers (1967) and Doedens & Ibers (1967). Experimental procedures, if not stated, and a list of computer programs used in the course of the work are given by Baur & Khan (1970).

In Laue group 2/*m* there are four equivalent reflections: $hkl,\bar{h}\bar{k}\bar{l}$, $h\bar{k}l$ and $\bar{h}k\bar{l}$. Of these, the hkl and $\bar{h}k\bar{l}$ reflections were collected between 0 and 40° in 2θ, and a third set of $\bar{h}\bar{k}\bar{l}$ reflections was collected between 0 and 33° in 2θ since there were only few reflections with significant intensities at 2θ-angles higher than 33°. The total number of intensities collected was 8148.

After correction for Lorentz–polarization effects equivalent reflections were sorted together and the individual values of the squared structure amplitudes and their standard deviations were averaged. If the range of intensities of equivalent reflections exceeded the standard deviation by a factor greater than 2, the reflection was re-examined for possible machine malfunctions. A total of 2981 unique structure amplitudes were obtained in this manner, 887 of them were zero or smaller than 1·5 times their standard deviation in which case they were considered to be zero.

Crystal data

The crystals were lath-like in shape and elongated parallel to [100]. Zero and upper level precession photographs around [010] and [001] indicated monoclinic symmetry; systematically absent reflections were *hkl* for $h+k$ odd and *h*0*l* for *l* odd. These absences are consistent with space groups *Cc* and *C*2/*c*. The final results point to *C*2/*c* as the true space group for $Ba_6Ti_{17}O_{40}$.

Preliminary cell constants were obtained from the photographs and later refined by the least-squares method using 22 reflections which had been centered on the automatic X-ray diffractometer. They are $a=9{\cdot}883$ (6), $b=17{\cdot}08$ (1), $c=18{\cdot}92$ (1) Å, $\beta=98°42'$ (2), $V=3156$ (4) Å^3. The unit-cell contains $Z=4$ formula units $Ba_6Ti_{17}O_{40}$, the calculated density is $D_x=4{\cdot}80$ g.cm^{-3}.

Solution of the structure and refinement

The positions of the barium atoms were derived from the Patterson function and refinement was tried in space group *C*2/*c* using 721 reflections of low θ. The function minimized was $\sum w(|F_o|-|F_c|)^2$ where $|F_o|$ and

Table 2. $Ba_6Ti_{17}O_{40}$, *positional and thermal parameters*

The *x*,*y*,*z* are fractions of the cell edges, the *B* are in Å^2. In parentheses are the estimated standard deviations in units of the last significant digits.

	Position	*x*	*y*	*z*	*B*
Ba(1)	8(*f*)	0·06961 (12)	0·08981 (7)	0·44274 (6)	0·77 (3)
Ba(2)	8(*f*)	0·86257 (12)	0·42547 (7)	0·82157 (6)	0·82 (3)
Ba(3)	8(*f*)	0·85369 (12)	0·28319 (7)	0·31496 (6)	0·85 (3)
Ti(1)	4(*e*)	0	0·1040 (3)	0·25	0·53 (9)
Ti(2)	4(*e*)	0	0·9378 (3)	0·25	0·35 (8)
Ti(3)	8(*f*)	0·7227 (3)	0·9011 (2)	0·8618 (2)	0·26 (6)
Ti(4)	4(*e*)	0	0·7476 (3)	0·25	0·35 (8)
Ti(5)	8(*f*)	0·7041 (4)	0·9257 (2)	0·3697 (2)	0·46 (6)
Ti(6)	8(*f*)	0·7097 (3)	0·7527 (2)	0·3736 (2)	0·23 (6)
Ti(7)	8(*f*)	0·9777 (3)	0·1599 (2)	0·8816 (2)	0·34 (6)
Ti(8)	4(*c*)	0·25	0·25	0	0·27 (8)
Ti(9)	8(*f*)	0·9669 (3)	0·3241 (2)	−0·0011 (2)	0·26 (6)
Ti(10)	8(*f*)	0·2560 (3)	0·4199 (2)	0·0135 (2)	0·21 (6)
Ti(11)	4(*b*)	0	0·5	0	0·49 (9)
O(1)	8(*f*)	0·9310 (13)	0·0803 (7)	0·5594 (6)	0·5 (3)
O(2)	8(*f*)	0·9390 (13)	0·2415 (7)	0·5530 (7)	0·8 (3)
O(3)	8(*f*)	0·9395 (13)	0·4120 (7)	0·5542 (7)	0·7 (3)
O(4)	8(*f*)	0·2049 (12)	0·0156 (7)	0·0672 (6)	0·2 (3)
O(5)	8(*f*)	0·1883 (12)	0·1586 (7)	0·5748 (6)	0·2 (3)
O(6)	8(*f*)	0·1852 (12)	0·3225 (7)	0·5674 (6)	0·3 (3)
O(7)	8(*f*)	0·1775 (12)	0·4950 (7)	0·0605 (6)	0·7 (3)
O(8)	8(*f*)	0·9263 (14)	0·4131 (8)	0·0582 (7)	1·1 (3)
O(9)	8(*f*)	0·9300 (13)	0·2532 (7)	0·0698 (7)	0·7 (3)
O(10)	8(*f*)	0·1772 (12)	0·3303 (7)	0·0558 (7)	0·6 (3)
O(11)	8(*f*)	0·2074 (12)	0·1642 (7)	0·0616 (6)	0·1 (3)
O(12)	8(*f*)	0·9011 (13)	0·0183 (8)	0·1965 (7)	0·8 (3)
O(13)	8(*f*)	0·9085 (12)	0·1621 (7)	0·6900 (6)	0·1 (3)
O(14)	8(*f*)	0·8901 (13)	0·3272 (8)	0·6925 (7)	1·2 (3)
O(15)	8(*f*)	0·8713 (13)	0·4869 (8)	0·6821 (7)	0·7 (3)
O(16)	8(*f*)	0·1223 (12)	0·0802 (7)	0·6776 (6)	0·5 (3)
O(17)	8(*f*)	0·1293 (13)	0·2421 (8)	0·6801 (7)	0·8 (3)
O(18)	8(*f*)	0·8759 (12)	0·3410 (7)	0·1795 (7)	0·3 (3)
O(19)	8(*f*)	0·8842 (12)	0·1803 (7)	0·1899 (6)	0·4 (3)
O(20)	8(*f*)	0·1287 (13)	0·1137 (8)	0·1785 (7)	1·2 (3)

$|F_c|$ are the observed and calculated structure amplitudes and w the weight. At this stage all reflections were given unit weight. Later w was taken as $1/\sigma^2(F_o^2)$. Atomic scattering factors for Ti^{2+}, O^{1-} and Ba were taken from *International Tables for X-ray Crystallography* (1962).

Six cycles of Fourier synthesis and structure factor calculations gave a complete model of the structure which refined in four cycles to a discrepancy index of 7·8%. An extinction correction using Zachariasen's (1963*a*) formula ($C=0{\cdot}0023$) was applied and refinement ended after three cycles with an R value of 6·0% for 2094 observed data and 13·3% for all 2981 reflections.

A refinement of the final atomic coordinates in the acentric space group Cc led to a lower R value of 5·5% but oscillations of atomic parameters and large standard deviations showed that the convergence of the refinement was poor and resulted in unreliable parameters. Since no effects of anomalous dispersion could be detected and the centric structure was chemically more reasonable than the acentric one, space group $C2/c$ is to be preferred as the true space group of $Ba_6Ti_{17}O_{40}$.

The final difference synthesis showed as highest peaks electron densities of 4 e.Å^{-3} near the positions of the barium atoms, thus confirming the chemical formula $Ba_6Ti_{17}O_{40}$.

Barium and oxygen atoms are arranged approximately in close-packed layers perpendicular to the [103] direction. Such an arrangement contains false centers of symmetry which are not crystallographic centers since the close-packed layers consist of two kinds of atoms. Thus, the final structure has a false center of symmetry in 0·85,0,0·56 which in the beginning led to some difficulty in interpreting the Patterson function.

Table 1 gives the values of $|F_o|$ and F_c, based on $Ba_{12}Ti_{34}O_{80}$. The 887 unobserved reflections are not included. The final atomic parameters and their estimated standard deviations are given in Table 2.

Description of the crystal structure

Coordination octahedra around atoms Ti(8), Ti(9), Ti(10) and Ti(11) share edges to form ribbons of composition Ti_3O_{10}. They extend in direction [$\bar{1}$10] at height $z=0$ (Fig. 1) and have a width of alternately one and two octahedra. The same type of ribbons extend in the [110] direction at height $z=0{\cdot}5$; they are related to the former by the twofold axis and are connected to each other *via* clusters of coordination octahedra of composition $Ti_{11}O_{40}$. The clusters are arranged around the twofold axes. Atoms Ti(1), Ti(2) and Ti(4), situated on the twofold axis, are the cores of these clusters: they share edges with each other, are of composition Ti_3O_{14} and are at height $z=0{\cdot}25$ (Fig. 2). Above and below the string of Ti(1), Ti(2) and Ti(4) octahedra, at heights $z=0{\cdot}12$ and 0·38 and

Table 3. *Comparison of pseudohexagonal cells for several barium titanates and olivine*

	a	*b*	*c*	α	β	γ	$\frac{2c}{a+b}$	Thickness of 1 layer in *c*	Thickness of 1 atom in *a,b*	$\frac{1 \text{ layer}}{1 \text{ atom}}$
Ideal h.c.p.	—	—	—	90·0°	90·00°	120·00°	1·63	—	—	0·816
$Ba_6Ti_{17}O_{40}$	17·08 Å	17·11 Å	56·11 Å	90·0	88·85	119·95	3·28	2·34 Å	2·85 Å	0·821
$BaTi_5O_{11}$	23·15	22·75	14·02	90·0	90·00	119·90	0·61	2·34	2·87	0·815
$BaTiO_3$(c)	2·84	2·84	6·96	90·0	90·00	120·00	2·45	2·32	2·84	0·816
$BaTiO_3$(h)	5·73$_5$	5·73$_5$	14·05	90·0	90·00	120·00	2·45	2·34	2·87	0·817
Olivine	12·02	11·92$_5$	4·78	90·0	90·00	120·30	0·40	2·39	2·99	0·798

	Pseudohexagonal cell in terms of original cell	Sequence of layers	Reference
Ideal h.c.p.	— — —	*AB*	—
$Ba_6Ti_{17}O_{40}$	$\frac{3}{2}\frac{\bar{1}}{2}0/010/103$	*ABCACABCBCABABCACABCBCAB*	This work
$BaTi_5O_{11}$	$\bar{3}0\bar{1}/103/010$	*ABCACB*	Tillmanns (1969)
$BaTiO_3$(*c*)	$\frac{1}{2}\frac{\bar{1}}{2}0/\frac{\bar{1}}{2}0\frac{1}{2}/111$	*ABC*	Evans (1961)
$BaTiO_3$(*h*)	$\bar{1}00/0\bar{1}0/001$	*ABCACB*	Burbank & Evans (1948)
Olivine	$100/\bar{1}01/010$	*AB*	Hanke (1965)

related by the twofold axis, are two groups of four octahedra each. These groups consist of the coordination octahedra around atoms Ti(3), Ti(5) and Ti(6) arranged as a column of three edge-sharing octahedra parallel to [010], which shares only corners with the column situated on the twofold axis, and of the co-

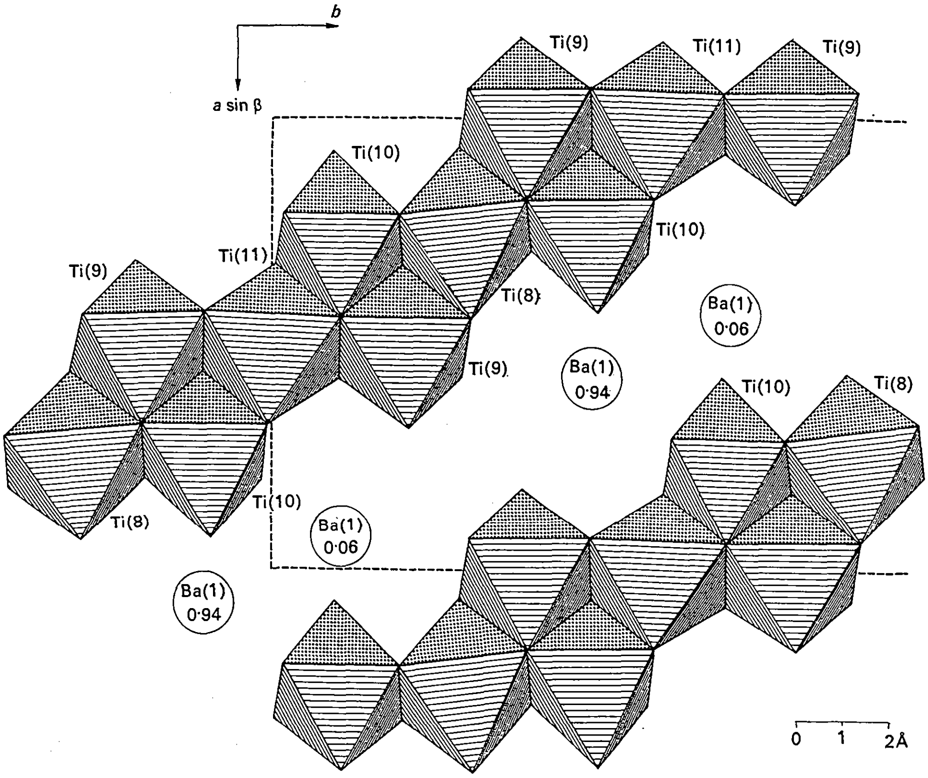

Fig. 1. Ribbons of coordination octahedra around titanium atoms 8, 9, 10 and 11 of composition Ti_3O_{10}. Titanium atoms are at $z \simeq 0$; the height of the barium atoms is in fractions of the c cell-edge. Projection along [001]. The angle between [001] and the normal to the close-packed layers is 10°.

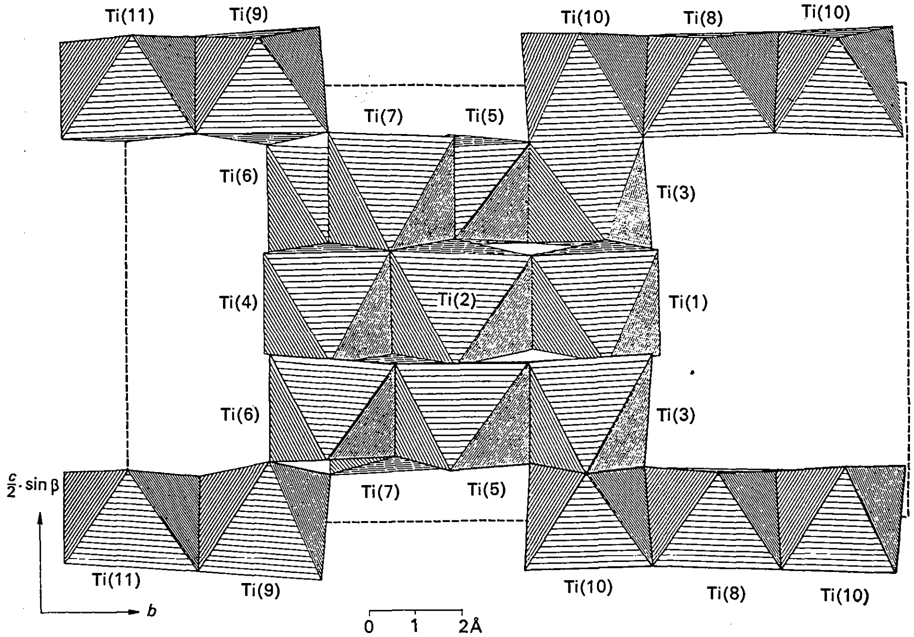

Fig. 2. Connection between Ti_3O_{10}-ribbons at $z=0$ and 0·5 *via* clusters of coordination octahedra of composition $Ti_{11}O_{40}$. Octahedra with light, medium and heavy lines are at $x \simeq 0·2$, 0·5, 0·8 respectively. For clearness not all octahedra are drawn. Projection along [100].

Table 4. *Interatomic distances and ζ-values of the oxygen atoms*

O–O distances which do not belong to the same coordination octahedron are marked with an asterisk. Titanium atoms in special positions are coordinated twice by the same oxygen atom and the Ti–O distance is given twice. These oxygen atoms however are only once coordinated by the titanium atom in the special position. Standard deviations are approximately: 0·012 for Ba–O and Ti–O, 0·015 for O–O, 0·002 for Ba–Ba, 0·003 for Ba–Ti and 0·005 Å for Ti–Ti distances.

1.67	2.00	2.85	2.33	2.17	1.68	1.68	2.00	1.68	2.18	2.35	1.68	2.18	1.88	1.70	2.00	2.36	1.70	2.05	1.86	ζ
O(1)	O(2)	O(3)	O(4)	O(5)	O(6)	O(7)	O(8)	O(9)	O(10)	O(11)	O(12)	O(13)	O(14)	O(15)	O(16)	O(17)	O(18)	O(19)	O(20)	
2.91 2.77			3.10 2.98	2.85	2.88	2.99		2.80		3.01	2.96							3.04	2.81	Ba(1)
		2.83			2.83	2.69					2.75		3.01 3.01	2.85 2.84		3.13		3.02	3.35	Ba(2)
								2.86	2.64	3.22		2.74	3.05			3.15	2.84 2.79	3.14 3.00	2.90	Ba(3)
											1.96 1.96							1.98 1.98	2.00 2.00	Ti(1)
											1.89 1.89	2.17 2.17			1.98 1.98					Ti(2)
		2.43	2.01							1.88			1.88	1.86					1.77	Ti(3)
												2.04 2.04	1.91 1.91			1.98 1.98				Ti(4)
			2.07	1.99			2.03							1.88	2.05		1.83			Ti(5)
				1.99	1.90			1.87								2.01	1.93	1.87		Ti(6)
1.90	1.96			1.94								1.89			1.94	2.02				Ti(7)
	1.99 1.99								1.94 1.94	1.96 1.96										Ti(8)
	2.02	2.10			1.81		1.97	1.88	2.19											Ti(9)
1.81		2.15	1.97			1.80			1.94	2.09										Ti(10)
		1.96 1.96				1.95 1.95	2.05 2.05													Ti(11)
	2.76	3.96	2.79 *3.15	2.85		2.82			2.93	2.87	*3.14	2,87			2.70	3.92				O(1)
	3.98	2.91		2.82	2.78		3.95	2.83	2.87 2.67	2.82 2.76		2.98	*3.12		3.89	2.82				O(2)
		3.93	2.67		2.85	2.70 2.83	2.67 2.99	3.93	2.62	2.66			3.09	2.90					4.16	O(3)
				2.98		2.84	2.83		3.81	2.54			3.86	2.52	2.87		3.90		2.88	O(4)
					2.80 *3.15		2.71	2.84 *3.24				3.77		3.86	2.53	2.59	2.50	3.85		O(5)
						*3.12	2.91	2.74 2.92	3.97							2.66	3.83	2.80		O(6)
						3.89	2.84 2.81		2.81	3.85	*3.15									O(7)
							4.09	2.74	2.86					3.01	4.02		2.72			O(8)
									2.82	*3.16						3.88	2.68	2.69		O(9)
									3.87	2.65 2.85		*3.15								O(10)
										3.92			2,84	3.66					2.60	O(11)
											2.59	4.05 3.08			2.82 2.95			2.77 3.92	2.84 2.92	O(12)
												2.68	2.83 3.94		2.57 2.92	2.61 2.89				O(13)
													2.83	2.74		2.82 2.85			2.75	O(14)
														*3.33	2.92		2.94		2.94	O(15)
															3.92	2.77	2.84		*3.31	O(16)
																3.95	2.82	2.83		O(17)
																	*3.34	2.75		O(18)
																		2.97	2.71 2.76	O(19)
																			3.98	O(20)

Ba(1)	4.111													
Ba(2)	3.964	4.115												
Ba(3)	4.444		4.068											
Ti(1)	3.615	3.669	3.675											
Ti(2)	4.444	4.319	4.405	2.838										
Ti(3)	3.541	3.468 3.550	3.565											
Ti(4)		3.602	3.578		3.249									
Ti(5)	3.907	4.389 4.213	4.224 4.231			2.970								
Ti(6)	3.453	3.600	3.564 3.565					2.955						
Ti(7)	3.628		4.215		3.034 3.034		2.984 2.984	3.052	3.023					
Ti(8)	4.435		3.835											
Ti(9)	4.177 4.181	3.777	3.760								3.068 3.068			
Ti(10)	3.560 3.412	4.380	4.269			2.857					2.913 2.913	3.268		
Ti(11)		3.670										3.022	2.854	
	Ba(1)	Ba(2)	Ba(3)	Ti(1)	Ti(2)	Ti(3)	Ti(4)	Ti(5)	Ti(6)	Ti(7)	Ti(8)	Ti(9)	Ti(10)	Ti(11)

ordination octahedron around Ti(7) which shares edges with both types of columns (Figs. 2 and 3). The clusters share with the ribbons several octahedral elements: two faces [the Ti(3) and Ti(10) octahedra share one face] and 10 additional corners. Table 6 lists the elements which are shared between various octahedra. The barium atoms are situated in the voids of this framework structure and have coordination numbers of 12 for Ba(1) and of 11 for Ba(2) and Ba(3).

An alternate way of looking at the crystal structure is to regard it as a close-packed array of oxygen and barium atoms in which some of the octahedral voids are filled by titanium atoms. It is apparent that all oxygen and barium atoms have z parameters with the approximate values 0·06, 0·19, 0·31, 0·44, 0·56, 0·69, 0·81 and 0·94. Of these eight layers only two are crystallographically distinct; the other six are related to the first two by the twofold axes at $z=\frac{1}{4}$ and $\frac{3}{4}$ and by the centers of symmetry at $z=0$ and 0·5. The layer at $z=0{\cdot}06$ (Fig. 1) consists of oxygen atoms one through eleven and of Ba(1); the layer at $z=0{\cdot}19$ or $z=0{\cdot}31$ (Fig. 3) consists of oxygen atoms twelve through twenty, Ba(2), Ba(3) and one void [between Ba(2) and Ba(3) there is no oxygen atom]. Within these layers with near-equal z values the arrangement is close-packed. The nearly hexagonal layers are stacked along [103] in the sequence *ABCACABCBCABABCACABCBCAB*. The crystallographic identity period of the packing of the complete structure is 24 layers. If one views just the packing of the barium and oxygen atoms the identity period is only 12 layers. Of course one unit-cell repeats itself after 8 layers, but since the direction of packing is [103] a crystallographically identical point is reached only after three unit cells. The angle between [103] and the normal to (001) (*i.e.* **c***) is 1·33°. The titanium atoms occupy 17 of the 18 octahedral voids which are coordinated by oxygen atoms only. The remaining site is not occupied presumably because it would mean the sharing of *two* octahedral faces with the adjoining Ti(6) coordination octahedra.

The transformation matrix between one of the several possible pseudohexagonal (*ph*) unit-cells and the monoclinic one is ($\frac{3}{2}\,\overline{\frac{1}{2}}\,0/010/103$). The resulting unit-cell parameters are: $a_{ph}=17{\cdot}08$, $b_{ph}=17{\cdot}11$, $c_{ph}=56{\cdot}11$ Å, $\alpha_{ph}=90{\cdot}0$, $\beta_{ph}=88{\cdot}85$, $\gamma_{ph}=119{\cdot}95°$. The c/a ratio (averaged over a_{ph} and b_{ph}) is 3·283; for an ideal close-packed structure one would expect this value to be 3·266 [$=\sqrt{(32/3)}$].

The geometry of the pseudohexagonal unit-cell conforms surprisingly well with the close-packed arrangement. The detailed atomic positions of the individual atoms on the other hand deviate from the ideal close-packed structure by several tenths of one Ångström. The data for several other barium titanates are presented in Table 3. It is remarkable how constant the values of the thickness of one pseudohexagonal layer and of the average atom-to-atom distance within one layer are. The c/a ratio (1 layer/1 atom) for these compounds is very close to the ideal value for a close-packed arrangement. For comparison the corresponding data of olivine $(Mg_{0{\cdot}9}Fe_{0{\cdot}1})_2SiO_4$ are given in the Table: the c/a ratio is in this case not quite so close to the ideal value.

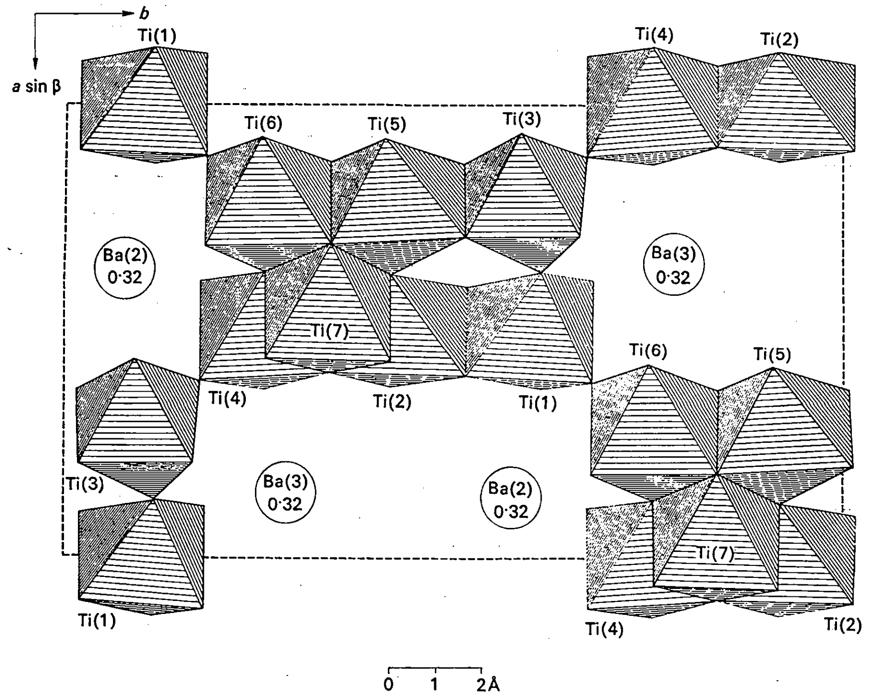

Fig. 3. Connection between coordination octahedra around Ti(1), Ti(2), Ti(4) situated on the twofold axis at $z=0{\cdot}25$ and Ti(3), Ti(5), Ti(6) and Ti(7) at $z\simeq0{\cdot}38$. As in Fig. 2 not all octahedra are drawn. Projection along [001].

The Ba(1) atom is located in the middle layer of a hexagonal *BAB* sequence with an icosahedral 12-coordination. The other two barium atoms in the middle of a cubic *ABC* sequence are both in 11-coordinations which are simply cuboctahedra with one of the coordinating oxygen atoms missing. These descriptions are of course idealized. As one can gather from Table 4, the Ba–O distances range in length from 2·64 to 3·35 Å, and therefore the coordination polyhedra must be appreciably distorted. The average of all 34 crystallographically different Ba–O distances is 2·93 Å. The distortions of the octahedral coordinations around the Ti atoms are very pronounced and larger than in any other accurately determined titanate crystal structure. The bond lengths Ti–O range from 1·77 to 2·43 Å, the octahedral angles which should ideally be 90° scatter between 73·3 and 108·1°, while the angles which should be 180° can be as small as 153·9° (Table 5). The average values of the Ti–O distances within each octahedron are listed in Table 6: they are of the expected lengths, close to the averages found in rutile and brookite (Baur, 1956, 1961*a*).

It is interesting to note that the Ti(3)–Ti(10) distance of 2·857 Å across the shared octahedral face is not the shortest Ti–Ti distance occurring in Ba$_6$Ti$_{17}$O$_{40}$. The distances Ti(1)–Ti(2) of 2·838 Å and Ti(10)–Ti(11) of 2·854 Å, which are across shared edges are even shorter. The coordination numbers of the oxygen atoms vary from 3 to 6 (Tables 4 and 7). Seven different coordinations of the oxygen atoms can be distinguished according to the number of titanium and barium atoms which are surrounding them.

Table 5. *Bond angles around the titanium atoms*

Standard deviations are approximately 0·5°.

O(12)	83.1			O(12)	O(13)	O(13)	O(16)	O(16)	Ti(2)
O(19)	89.7	172.7		86.7	173.4	98.7	93.6	99.4	O(12)
O(19)	172.7	89.7	97.5		98.7	173.4	99.4	93.6	O(12)
O(20)	95.3	91.8	85.9	87.8		76.3	76.5	89.4	O(13)
O(20)	91.8	95.3	87.8	85.9	170.5		89.4	76.5	O(13)
Ti(1)	O(12)	O(12)	O(19)	O(19)	O(20)			162.2	O(16)

O(4)	73.3			O(13)	O(14)	O(14)	O(17)	O(17)	Ti(4)
O(11)	75.1	81.5		82.0	171.3	91.3	80.7	91.6	O(13)
O(14)	90.8	163.6	98.1		91.3	171.3	91.6	80.7	O(13)
O(15)	84.1	81.0	155.9	94.1		95.9	92.8	94.1	O(14)
O(20)	164.6	98.9	90.9	97.5	108.1		94.1	92.8	O(14)
Ti(3)	O(3)	O(4)	O(11)	O(14)	O(15)			169.8	O(17)

O(5)	94.6			O(6)	O(9)	O(17)	O(18)	O(19)	Ti(6)
O(8)	87.4	84.9		92.0	94.5	80.4	79.1	169.6	O(5)
O(15)	79.3	171.2	101.1		93.0	85.6	171.0	95.9	O(6)
O(16)	88.2	77.3	161.2	96.0		174.7	89.5	91.8	O(9)
O(18)	175.2	81.5	89.3	104.9	93.8		91.2	93.4	O(17)
Ti(5)	O(4)	O(5)	O(8)	O(15)	O(16)			92.7	O(18)

O(2)	91.3			O(2)	O(10)	O(10)	O(11)	O(11)	Ti(8)
O(5)	95.7	92.4		180.0	94.1	85.9	91.4	88.6	O(2)
O(13)	98.8	101.5	159.6		85.9	94.1	88.6	91.4	O(2)
O(16)	89.5	173.6	81.3	84.6		180.0	85.7	94.3	O(10)
O(17)	176.9	90.2	81.5	83.6	88.7		94.3	85.7	O(10)
Ti(7)	O(1)	O(2)	O(5)	O(13)	O(16)			180.0	O(11)

O(3)	89.9			O(3)	O(4)	O(7)	O(10)	O(11)	Ti(10)
O(6)	92.7	93.4		171.4	95.1	102.4	102.3	94.3	O(1)
O(8)	164.6	82.1	100.8		80.7	85.7	79.4	77.5	O(3)
O(9)	92.9	161.5	104.8	90.7		97.7	153.9	77.5	O(4)
O(10)	78.5	75.3	165.5	86.7	87.3		97.3	163.1	O(7)
Ti(9)	O(2)	O(3)	O(6)	O(8)	O(9)			82.0	O(10)

O(3)	180.0						
O(7)	87.4	92.6					
O(7)	92.6	87.4	180.0				
O(8)	83.5	96.5	90.8	89.2			
O(8)	96.5	83.5	89.2	90.8	180.0		
Ti(11)	O(3)	O(3)	O(7)	O(7)	O(8)		

Table 6. *Average* Ti–O *distances and common elements of the coordination octahedra*

Ti-atom number	Symmetry of Ti-site	Average Ti–O distance	Number of Ti-atom coordination octahedra with which are shared: faces	edges	corners	Total of shared elements
1	2	1·977 Å		2	3, 3, 6, 6	5
2	2	2·014		1, 4, 7, 7	5, 5	6
3	1	1·972	10	5	1, 4, 8, 9, 11	7
4	2	1·977		2, 7, 7	3, 3, 6, 6	7
5	1	1·974		3, 6, 7	2, 9, 10, 11	7
6	1	1·931		5, 7	1, 4, 9, 9	6
7	1	1·941		2, 4, 5, 6	8, 9, 10	7
8	$\bar{1}$	1·960		9, 9, 10, 10	3, 3, 7, 7	8
9	1	1·995		8, 10, 11	3, 5, 6, 6, 7	8
10	1	1·962	3	8, 9, 11	5, 7	6
11	$\bar{1}$	1·986		9, 9, 10, 10	3, 3, 5, 5	8
Mean		1·972				

Table 7. *Coordinations of oxygen atoms*

Number of coordinated titanium atoms	Number of coordinated barium atoms	Total number of coordinated cations	Number of oxygen atoms so coordinated
2	2	4	7
2	3	5	2
2	4	6	1
3	0	3	3
3	1	4	3
3	2	5	3
4	1	5	1

It has been shown previously (Baur, 1961*b*) that the bond lengths vary with ζ: oxygen atoms which are oversaturated (have a high ζ-value) form bonds which are longer than the average bond length for this coordination polyhedron, while oxygen atoms which are undersaturated form shorter bonds to the cations. We used Ti–O bond lengths from this structure determination, from $BaTi_5O_{11}$ (Tillmanns, 1969) and $K_2Ti_6O_{13}$ (Cid-Dresdner & Buerger, 1962) to calculate a weighted least-squares linear regression between the Ti–O bond lengths and the corresponding ζ-values (ζ is used here as defined by Pauling, 1960). The Ti–O bond lengths used for the calculation were averaged over all the titanium bonds formed by each oxygen atom. The values of the intercept and the slope were found to be 1·552(16) and 0·200(8). The correlation coefficient between ζ and $d_{\mathrm{Ti\text{-}O}}$ is 0·94. For a sample size of 38 this is highly significant. Using the expression $d_{\mathrm{Ti\text{-}O}} = 1{\cdot}552 + 0{\cdot}200\zeta$ we calculated the predicted mean bond-length from an oxygen atom to its surrounding titanium atoms (Table 8). The largest differences between observed and predicted bond lengths are 0·06 Å. It must be emphasized that we are dealing here with the mean values. For the O(3) oxygen atom the mean value of the four Ti –O bonds formed is 2·16 Å. The individual bonds are 2·43, 2·15, 2·10 and 1·96 Å. The prediction is meaningful for the average bond length, but of limited value for the individual distances. These individual atomic distances may be influenced by surrounding atoms which are not involved in that bond itself. A similar regression analysis using the individual distances resulted in values for the intercept and the slope of 1·558(45) and 0·198(21), the correlation coefficient is 0·69, the sample size is 100. At this point one could introduce a bond order–bond length relationship as done by Zachariasen (1963*b*) for B–O bonds. In this case however, we feel that this would not be meaningful for the purpose of predicting bond lengths because the bond orders would be derived from the bond lengths. Therefore we could not predict individual bond lengths unless we wished to indulge in circular reasoning. The relation between bond length and ζ in many similar crystal structures will be discussed in a forthcoming paper (Baur, 1970)

One of us (E.T.) thanks the Heinrich-Hertz-Stiftung, Düsseldorf, Germany, for a travel grant. We are grateful to Dr Richard McCammon for the program to calculate the linear least-squares fit. The computing facilities used in this work were supported partly by N.S.F. grant No. GP-7275, the experimental apparatus was purchased with funds from N.S.F. grant No. GA-314 and the Research Board of the University of Illinois at Chicago Circle.

Table 8. *Observed and predicted mean bond lengths of* Ti–O *bonds in* $Ba_6Ti_{17}O_{40}$

Ti–O bonds around	$d_{\mathrm{Ti-O}}$ observed	$d_{\mathrm{Ti-O}}$ predicted
O(1)	1·86 Å	1·89 Å
O(2)	1·99	1·95
O(3)	2·16	2·12
O(4)	2·02	2·02
O(5)	1·98	1·99
O(6)	1·86	1·89
O(7)	1·88	1·89
O(8)	2·01	1·95
O(9)	1·88	1·89
O(10)	2·02	1·99
O(11)	1·97	2·02
O(12)	1·92	1·89
O(13)	2·03	1·99
O(14)	1·90	1·93
O(15)	1·87	1·89
O(16)	1·99	1·95
O(17)	2·01	2·03
O(18)	1·83	1·89
O(19)	1·92	1·96
O(20)	1·89	1·93

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