JOURNAL OF SOLID STATE CHEMISTRY 6, 378–383 (1973)

Prototype Structure of $Pb_5Ge_3O_{11}$*

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Received July 10, 1972

The prototypic structure of the optically active ferroelectric $Pb_5Ge_3O_{11}$ has been deduced from packing considerations and refined from single-crystal diffractometer data. Interleaving segments of the apatite and nasonite structures in layers perpendicular to c gives the lead germanate structure. The space group of the prototype is $P\bar{6}$, with $a = 10.190$, $c = 10.624$ Å, and $Z = 3$. Atomic coordinates were refined to give an R-factor of 0.093 using 463 X-ray reflections. The structure contains tetrahedral GeO_4 groups and double tetrahedral Ge_2O_7 groups in equal numbers. Lead is found in both trigonal pyramid and trigonal prism configurations.

Lead germanate ($Pb_5Ge_3O_{11}$) has attracted considerable interest because it is both ferroelectric (*1*, *2*) and optically active (*3*, *4*). Below the Curie temperature of 177°C, the optical handedness inverts when the spontaneous polarization is reversed by an applied electric field. Unlike most ferroelectrics, 180° domains are clearly visible because of the optical rotatory power of 5.6°/mm for 5890 Å light. Using a modification of the Czochralski growth technique developed in Japan (*5*), we have grown clear transparent crystals exhibiting a well-defined domain structure (*6*). With limited-area switching, the domain states may prove useful for information storage and in the processing of light signals. Additional work on $Pb_5Ge_3O_{11}$ include studies of the piezoelectric and elastic properties (*7*), and the Raman spectrum (*8–10*) which shows an overdamped soft mode near the transition temperature. Based on physical properties, the Shuvalov symbol for the transition in lead germanate is $\bar{6}(1)D\bar{6}F3$.

Experimental Methods

A sphere of $Pb_5Ge_3O_{11}$ with a radius of 35 μm was ground from a fragment of a Czochralski-grown crystal using a compressed air grinder. Least-squares refinement of the orientation matrix yielded lattice parameters of $a = 10.190(6)$ and $c = 10.624(5)$ Å. The unit cell contains 3 formula units in a volume 955.3 Å^3, giving a calculated specific gravity of 7.41, slightly larger than the measured value of 7.33 (*5*). Intensity data for 463 reflections were collected using an automated diffractometer with a 2θ scan and filtered Mo$K\alpha$ radiation. Since there were no systematic absences, or superlattice reflections, the space group of the prototype structure is $P\bar{6}$ and that of the ferroelectric phase is $P3$. Standard reflections monitored periodically throughout data collection showed an extreme spread of 6% and a standard deviation from the mean of 1%. Intensities were corrected for absorption using the spherical correction factors given in Vol. 2 of the International Tables for X-Ray Crystallography. The maximum absorption correction (30.9) was less than three times the minimum (11.3).

A trial structure for $Pb_5Ge_3O_{11}$ was deduced from the apatite (*11*) and nasonite (*12*) structures. Cell constants and powder patterns for the three materials show a strong resemblance. The a dimension of all three cells is about 10 Å, while c is approximately 7 Å for apatite, 10 Å for lead germanate and 13 Å for nasonite. The apatite structure contains two layers of isolated tetrahedra related by a 6_3 screw axis parallel to c.

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* Sponsored by the Air Force Avionics Laboratory, Wright-Patterson Air Force Base, OH, under Contract F 33615-72-C-1632.

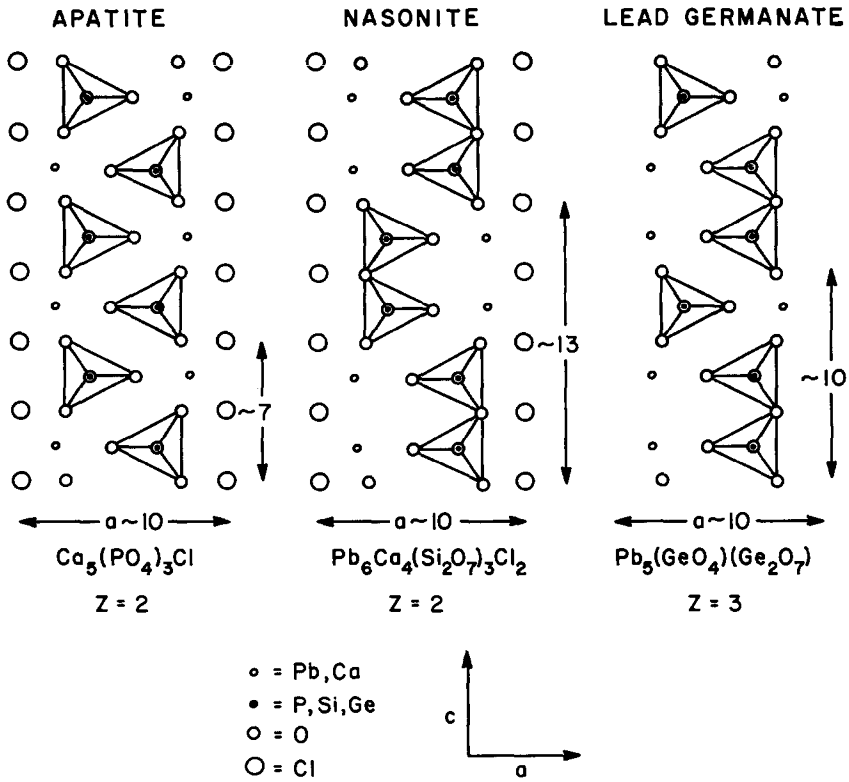

Fig. 1. Comparison of the idealized apatite, nasonite, and lead germanate structures showing a section parallel to (010) about 4 Å thick.

Nasonite has the same symmetry but contains double tetrahedra instead of discrete tetrahedra. Sections of the two structures are illustrated in Fig. 1. Combining half the apatite unit cell with half the nasonite cell gives the lead germanate structure, as shown in Fig. 1c. The trial model belonging to space group $P\bar{6}$ was confirmed by subsequent refinement.

The Bell-ORFLS (*13*) least-squares program was used for the structure refinement. There are 7 Pb, 5 Ge and 18 O coordinates to be refined in the $P\bar{6}$ prototype structure. Adding isotropic temperature factors for the 15 atoms in the asymmetric unit gives a total of 45 variable parameters in the least-squares refinement.

Beginning with the trial prototype structures derived from packing considerations, the Pb atomic coordinates were varied first, then the Ge coordinates, followed by Pb and Ge isotropic temperature factors. Next, all Pb and Ge parameters were varied simultaneously. The same procedure was used for oxygen coordinates and temperature factors. A least squares refinement varying all 45 parameters yielded an R-factor of 0.127. Isotropic temperature factors were converted to anisotropic form giving a total of 94 independent parameters. Two least-squares cycles gave an R-factor of 0.10. Two final cycles omitting 45 reflections below the observable limit yielded an R-factor of 0.093. Structure factors computed with the final coordinates are listed in Table I. There were no correlations involving atomic positions greater than 0.5. Anisotropic temperature factors for two of the atoms were not positive-definite but the discrepancies were within standard error. It is possible that the negative temperature factors reflect a systematic error such as absorption.

Since the orientation of a was arbitrarily assumed when the intensities were measured, the h and k indices of the reflections were interchanged to test the second possible orientation. Refined coordinates giving an agreement index of 0.093 for hkl reflections gave 0.136 for khl reflections after two least-squares cycles. Moreover, the new coordinates led to unacceptable interatomic distances, confirming the original choice of axes.

TABLE I

MEASURED AND CALCULATED STRUCTURE FACTORS OF $Pb_5Ge_3O_{11}$ AT 298 K[a]

h	k	l	$\lvert F_o \rvert$	$\lvert F_c \rvert$
0	0	1	*	56
0	0	2	*	91
0	0	3	431	440
0	0	4	157	172
0	0	5	133	108
0	0	6	811	872
0	0	7	177	161
0	0	8	*	67
0	0	9	133	90
0	1	0	*	90
0	1	1	24	42
0	1	2	*	59
0	1	3	276	273
0	1	4	47	43
0	1	5	60	54
0	1	6	88	84
0	1	7	90	81
0	1	8	60	77
0	1	9	144	132
0	2	0	*	373
0	2	1	36	47
0	2	2	61	58
0	2	3	139	168
0	2	4	116	99
0	2	5	85	81
0	2	6	184	205
0	2	7	84	92
0	2	8	67	80
0	2	9	96	121
0	3	0	836	848
0	3	1	40	51
0	3	2	54	50
0	3	3	49	41
0	3	4	52	28
0	3	5	65	51
0	3	6	506	530
0	3	7	60	45
0	3	8	69	37
0	3	9	88	68
0	4	0	*	318
0	4	1	89	79
0	4	2	69	91
0	4	3	563	562
0	4	4	148	135
0	4	5	149	134
0	4	6	195	165
0	4	7	175	195
0	4	8	*	187
0	4	9	247	230
0	5	0	*	24
0	5	1	64	27
0	5	2	49	51
0	5	3	356	385
0	5	4	78	61
0	5	5	65	65
0	5	6	<40	28
0	5	7	86	60
0	5	8	50	46
0	5	9	183	202
0	6	0	186	197
0	6	1	64	60
0	6	2	52	39
0	6	3	373	370
0	6	4	47	57
0	6	5	<40	11
0	6	6	160	171
0	6	7	72	54
0	6	8	<50	25
0	6	9	224	210
1	0	0	*	128
1	0	1	36	23
1	0	2	31	30
1	0	3	274	312
1	0	4	62	54
1	0	5	56	70
1	0	6	101	122
1	0	7	68	55
1	0	8	72	54
1	0	9	138	161
2	0	0	*	322
2	0	1	32	25
2	0	2	52	31
2	0	3	141	124
2	0	4	94	127
2	0	5	85	108
2	0	6	198	170
2	0	7	79	90
2	0	8	78	64
2	0	9	101	92
3	0	0	880	849
3	0	1	65	52
3	0	2	62	77
3	0	3	49	48
3	0	4	33	49
3	0	5	73	60
3	0	6	515	530
3	0	7	37	25
3	0	8	55	51
3	0	9	83	70
4	0	0	*	303
4	0	1	83	75
4	0	2	65	60
4	0	3	585	603
4	0	4	148	153
4	0	5	148	165
4	0	6	171	155
4	0	7	182	168
4	0	8	*	190
4	0	9	271	256
5	0	0	*	56
5	0	1	64	54
5	0	2	61	32
5	0	3	370	350
5	0	4	78	75
5	0	5	71	64
5	0	6	<50	63
5	0	7	81	79
5	0	8	49	53
5	0	9	177	173
6	0	0	205	203
6	0	1	64	69
6	0	2	45	38
6	0	3	374	356
6	0	4	67	49
6	0	5	56	50
6	0	6	175	175
6	0	7	72	49
6	0	8	<50	31
6	0	9	214	207
1	1	0	94	126
1	1	1	115	137
1	1	2	232	237
1	1	3	624	643
1	1	4	88	50
1	1	5	257	289
1	1	6	124	155
1	1	7	152	116
1	1	8	210	214
1	1	9	346	319
1	2	0	414	346
1	2	1	272	243
1	2	2	303	320
1	2	3	110	98
1	2	4	198	207
1	2	5	302	326
1	2	6	249	228
1	2	7	53	49
1	2	8	190	203
1	2	9	92	76
1	3	0	107	98
1	3	1	133	141
1	3	2	118	100
1	3	3	301	321
1	3	4	149	177
1	3	5	126	143
1	3	6	79	107
1	3	7	87	79
1	3	8	75	56
1	3	9	152	167
1	4	0	433	427
1	4	1	74	60
1	4	2	<40	32
1	4	3	235	235
1	4	4	67	91
1	4	5	<40	29
1	4	6	293	306
1	4	7	75	81
1	4	8	49	24
1	4	9	173	172
1	5	0	364	336
1	5	1	208	211
1	5	2	260	274
1	5	3	121	118
1	5	4	143	157
1	5	5	264	278
1	5	6	227	256
1	5	7	77	82
1	5	8	175	194
1	5	9	59	28
1	6	0	306	275
1	6	1	66	57
1	6	2	99	119
1	6	3	<40	48
1	6	4	69	61
1	6	5	105	130
1	6	6	210	216
1	6	7	67	69
1	6	8	136	144
1	6	9	<50	81
2	1	0	488	429
2	1	1	354	325
2	1	2	358	393
2	1	3	165	164
2	1	4	213	211
2	1	5	274	305
2	1	6	279	246
2	1	7	147	120
2	1	8	248	256
2	1	9	105	106
2	2	0	146	106
2	2	1	66	65
2	2	2	53	39
2	2	3	570	584
2	2	4	48	47
2	2	5	75	58
2	2	6	108	108
2	2	7	91	117
2	2	8	81	68
2	2	9	297	286
2	3	0	365	349
2	3	1	261	234
2	3	2	282	255
2	3	3	131	114
2	3	4	91	89
2	3	5	240	238
2	3	6	219	213
2	3	7	110	110
2	3	8	234	211
2	3	9	105	102
2	4	0	465	449
2	4	1	202	200
2	4	2	180	210
2	4	3	122	115
2	4	4	165	187
2	4	5	123	137
2	4	6	292	285
2	4	7	137	143
2	4	8	117	129
2	4	9	39	51
2	5	0	225	202
2	5	1	170	199
2	5	2	226	223
2	5	3	380	368
2	5	4	88	98
2	5	5	210	225
2	5	6	172	167
2	5	7	67	54
2	5	8	170	163
2	5	9	213	180
2	6	0	288	270
2	6	1	74	62
2	6	2	85	54
2	6	3	70	119
2	6	4	65	45
2	6	5	84	93
2	6	6	214	199
2	6	7	39	58
2	6	8	127	93
2	6	9	63	98
3	1	0	176	133
3	1	1	64	76
3	1	2	85	94
3	1	3	262	243
3	1	4	90	73
3	1	5	91	90
3	1	6	92	76
3	1	7	103	110
3	1	8	129	128
3	1	9	127	114
3	2	0	304	331
3	2	1	263	236
3	2	2	308	286
3	2	3	171	123
3	2	4	203	201
3	2	5	313	307
3	2	6	188	207
3	2	7	79	100
3	2	8	225	208
3	2	9	125	102
3	3	0	310	268
3	3	1	218	195
3	3	2	250	253
3	3	3	335	351
3	3	4	122	121
3	3	5	202	201
3	3	6	236	219
3	3	7	92	68
3	3	8	159	163
3	3	9	201	198
3	4	0	52	54
3	4	1	64	54
3	4	2	110	94
3	4	3	325	321
3	4	4	<40	14
3	4	5	98	76
3	4	6	<50	54
3	4	7	78	95
3	4	8	107	114
3	4	9	177	153
3	5	0	92	117
3	5	1	<40	51
3	5	2	48	47
3	5	3	314	343
3	5	4	71	45
3	5	5	84	82
3	5	6	<50	95
3	5	7	61	64
3	5	8	<50	48
3	5	9	165	181
3	6	0	85	90
3	6	1	223	209
3	6	2	253	250
3	6	3	403	415
3	6	4	132	147
3	6	5	243	223
3	6	6	98	64
3	6	7	100	76
3	6	8	195	188
4	1	0	423	369
4	1	1	67	38
4	1	2	<40	46
4	1	3	296	283
4	1	4	72	75
4	1	5	52	56
4	1	6	274	267
4	1	7	63	43
4	1	8	58	64
4	1	9	208	199
4	2	0	388	347
4	2	1	123	121
4	2	2	126	118
4	2	3	110	103
4	2	4	139	140
4	2	5	147	112
4	2	6	261	252
4	2	7	57	52
4	2	8	66	64
4	2	9	<50	46
4	3	0	83	108
4	3	1	88	108
4	3	2	80	91
4	3	3	317	318
4	3	4	127	139
4	3	5	103	131
4	3	6	57	80
4	3	7	94	77
4	3	8	101	90
4	3	9	161	166
4	4	0	578	573
4	4	1	85	70
4	4	2	83	37
4	4	3	56	49
4	4	4	128	99
4	4	5	119	117
4	4	6	407	408
4	4	7	148	153
4	4	8	133	130
4	4	9	84	74
4	5	0	165	168
4	5	1	<50	28
4	5	2	<50	44
4	5	3	78	57
4	5	4	<50	31
4	5	5	<50	44
4	5	6	125	136
4	5	7	<50	51
4	5	8	<50	54
4	6	0	233	262
4	6	1	60	59
4	6	2	<50	38
4	6	3	<50	74
4	6	4	93	75
4	6	5	<50	28
4	6	6	161	183
4	6	7	79	49
5	1	0	480	443
5	1	1	278	277
5	1	2	315	337
5	1	3	173	219
5	1	4	149	146
5	1	5	264	285
5	1	6	309	290
5	1	7	132	95
5	1	8	252	250
5	1	9	98	113
5	2	0	292	288
5	2	1	178	193
5	2	2	215	214
5	2	3	335	314
5	2	4	125	101
5	2	5	189	211
5	2	6	191	202
5	2	7	65	59
5	2	8	151	166
5	2	9	197	174
5	3	0	83	101
5	3	1	97	123
5	3	2	68	69
5	3	3	328	318
5	3	4	96	62
5	3	5	58	81
5	3	6	<50	61
5	3	7	86	105
5	3	8	76	64
5	3	9	164	158
5	4	0	149	147
5	4	1	105	95
5	4	2	97	95
5	4	3	126	178
5	4	4	85	65
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5	4	6	116	111
5	4	7	95	66
5	4	8	63	53
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5	5	2	208	223
5	5	3	896	895
5	5	4	98	71
5	5	5	213	240
5	5	6	158	174
5	5	7	61	53
5	6	0	161	172
5	6	1	115	98
5	6	2	127	138
5	6	3	71	54
5	6	4	106	105
5	6	5	121	124
6	1	0	293	254
6	1	1	72	63
6	1	2	110	120
6	1	3	<50	64
6	1	4	69	59
6	1	5	149	149
6	1	6	205	183
6	1	7	110	100
6	1	8	103	104
6	1	9	<50	61
6	2	0	247	251
6	2	1	85	66
6	2	2	90	81
6	2	3	76	64
6	2	4	82	70
6	2	5	111	117
6	2	6	170	187
6	2	7	75	95
6	2	8	100	101
6	2	9	71	73
6	3	0	134	120
6	3	1	209	195
6	3	2	238	245
6	3	3	405	412
6	3	4	142	144
6	3	5	205	203
6	3	6	107	79
6	3	7	105	78
6	3	8	175	167
6	4	0	191	183
6	4	1	67	45
6	4	2	74	71
6	4	3	<50	95
6	4	4	68	67
6	4	5	52	77
6	4	6	154	144
6	4	7	70	61
6	5	0	130	140
6	5	1	108	111
6	5	2	138	150
6	5	3	62	116
6	5	4	77	77
6	5	5	121	95
6	6	0	85	83
6	6	1	129	133

[a] Asterisks denote reflections omitted from least-squares refinement.

TABLE II

EQUIPOINTS, ATOMIC COORDINATES, AND ISOTROPIC TEMPERATURE FACTORS FOR THE LEAD GERMANATE STRUCTURE REFINED IN SPACE GROUP $P\bar{6}$[a]

Atom	Equipoint	x	y	z	B (Å^2)
Pb_1	6*l*	0.2622(5)	0.2628(5)	0.1849(4)	0.8(1)
Pb_2	2*h*	0.333	0.667	0.3382	−0.2(2)
Pb_3	2*i*	0.667	0.333	0.325(1)	2.4(3)
Pb_4	1*c*	0.333	0.667	0.000	1.0(2)
Pb_5	1*e*	0.667	0.333	0.000	2.2(3)
Pb_6	3*k*	0.249(1)	0.989(1)	0.500	2.1(2)
Ge_1	6*l*	0.015(1)	0.388(1)	0.152(1)	0.9(3)
Ge_2	3*k*	0.395(2)	0.389(2)	0.500	0.4(3)
O_1	6*l*	0.074(11)	0.330(8)	0.268	3.7(1.8)
O_2	6*l*	0.074(8)	0.581(9)	0.155(8)	3.7(1.5)
O_3	6*l*	0.818(16)	0.329(11)	0.195(11)	6.0(3.0)
O_4	3*j*	0.066(6)	0.347(7)	0.000	0.3(1.2)
O_5	3*k*	0.286(7)	0.481(8)	0.500	−0.8(1.5)
O_6	3*k*	0.584(10)	0.453(13)	0.500	2.9(2.1)
O_7	6*l*	0.302(16)	0.242(14)	0.377(8)	5.4(3.0)

[a] Standard errors associated with the final digit are given in parentheses.

Discussion

Atomic coordinates and isotropic temperature factors for $Pb_5Ge_3O_{11}$ are presented in Table II. The relatively high standard errors and large temperature factors no doubt arise partly because the refinement was carried out with low angle data in the prototype space group $P\bar{6}$, rather than using the true space group $P3$ and a more complete data set. Nevertheless, interatomic distances calculated with these coordinates indicate that the structure is satisfactory for the prototype model. Metal–oxygen distances are reasonable and the shortest O–O contact in the structure is 2.62 Å.

Table III lists the coordination number and average bond lengths for the metal atoms. Germanium atoms are in tetrahedral coordination with an average Ge–O distance of about 1.77 Å, in good agreement with the value 1.74 Å obtained from several well-refined structures containing GeO_4 tetrahedra (*14*). Lead atoms are found in threefold triangular pyramids and sixfold triangular prisms. Average Pb–O distances range from 2.23 to 2.86 Å. For comparison, in red PbO, lead forms tetragonal pyramids with an average interatomic distance of 2.30 Å (*15*), while in $PbTiO_3$ the average Pb–O distance is 2.81 Å (*16*).

Figures 2 and 3 show (001) sections of the GeO_4 and Ge_2O_7 layers corresponding to the apatite and nasonite segments of the structure. Open channels, similar to those found in several lead apatites, lie along the c axes.

We are presently collecting neutron diffraction data and high-angle X-ray intensities to refine the

TABLE III

METAL–OXYGEN BONDING IN THE PROTOTYPE STRUCTURE OF $Pb_5Ge_3O_{11}$

Atom	Oxygen coord. no.	Coord. polyhedron	Av bondlength (Å)
Pb_1	3	Triangular pyramid	2.23
Pb_2	3	Triangular pyramid	2.41
Pb_3	6	Triangular prism	2.33
Pb_4	6	Triangular prism	2.86
Pb_5	6	Triangular prism	2.60
Pb_6	6	Pentagonal pyramid	2.61
Ge_1	4	Tetrahedron	1.75
Ge_2	4	Tetrahedron	1.79

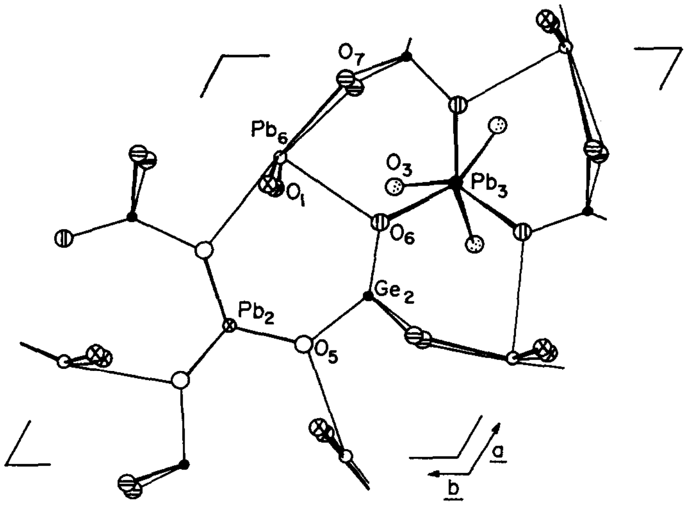

FIG. 2. Section of $Pb_5Ge_3O_{11}$ projected slightly off (001). The GeO_4 layer and interlayer lead coordination polyhedra are shown.

structure of the ferroelectric phase. Although it is premature to speculate on the atomic motions responsible for the spontaneous polarization and optical activity, one possible mechanism appears obvious. The lead atoms located in triangular prisms may shift along *c*, changing to triangular pyramid coordination. Such a motion would polarize the crystal along *c*, destroying the mirror plane perpendicular to *c* and lowering the symmetry from $\bar{6}(=3/m)$ to 3. Optical activity could result from accompanying motions of the neighboring oxygens. A shift in the Pb position along $+c$ would impart a clockwise twist to the germanium tetrahedra, giving rise to a handedness similar to quartz. A downward shift creates a counterclockwise twist, so that polarization reversal is accompanied by a change in handedness, and a change in sign of the optical activity coefficient.

Acknowledgments

We thank J. P. Dougherty, E. Sawaguchi, L. E. Cross, and D. K. Smith for their advice and assistance.

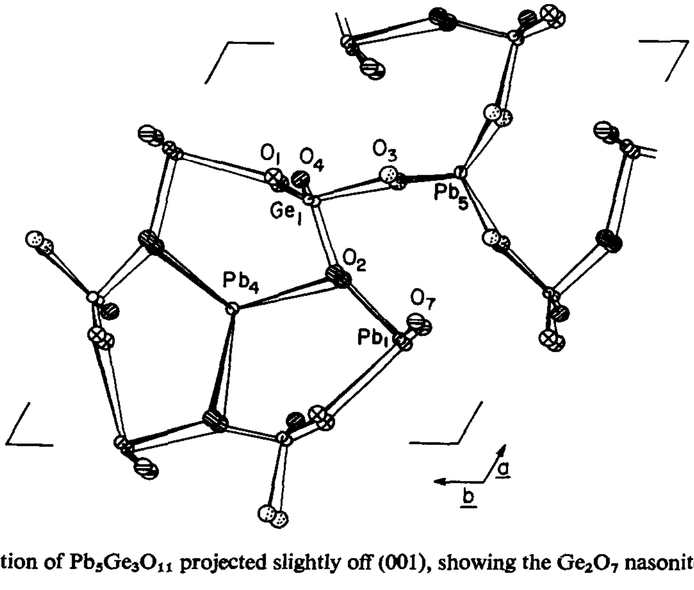

FIG. 3. Section of $Pb_5Ge_3O_{11}$ projected slightly off (001), showing the Ge_2O_7 nasonite-like layer.

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